MACRO

Non-equilibrio

↓

Forze termodinamiche e correnti

↓ (regime lineare ↓ Onsager)

Coefficienti di trasporto → Relazioni di Green Kubo

MICRO

Fluttuazioni

↓

Funzioni di correlazione dinamiche

↓ (regime lineare ↓ teor. di fluttuaz. dissipazione)

Funzioni di risposta → Relazioni di Green Kubo

TERMODINAMICA DI NON EQUILIBRIO

Sistemi macro → equilibrio

$$S = S(\underbrace{E, V, N}_{\text{estensive}}) \quad \rightarrow \quad \text{eq. fondamentale}$$

Eq. di stato : 1 componente → 2 eq. stato

$$\frac{1}{T} = \frac{\partial S}{\partial E} \qquad \frac{P}{T} = \frac{\partial S}{\partial V} \qquad -\frac{\mu}{T} = \frac{\partial S}{\partial N}$$

n variabili estensive X_i

$$S(X_1, \dots, X_n) \rightarrow Y_i = \frac{\partial S}{\partial X_i}$$

Y_i: variabili intensive coniugate a X_i

Es.: g.p. $PV = Nk_BT \qquad E = C_vT$

$$\frac{P}{T} = \frac{Nk_B}{V} \qquad \frac{1}{T} = \frac{C_v}{E}$$

Sistema composto : M sottosistemi

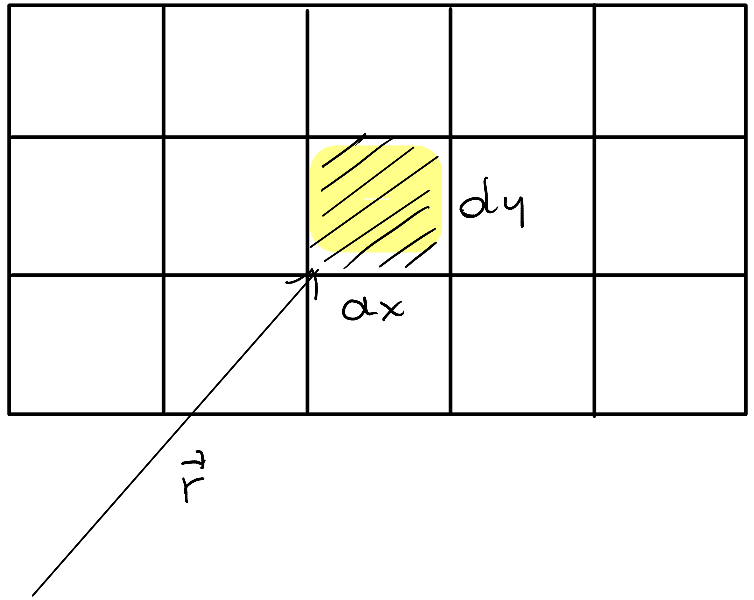
$$\boxed{1}\,\boxed{2}\,\cdots\,\boxed{M}$$

isolato

Postulato di Callen

S additiva sui sottosistemi. All'equilibrio, S ha un massimo rispetto alle ripartizioni delle X_i compatibili con i vincoli globali.

Equilibrio locale :



$\exists$ in $\forall \vec{r}$ un sottosistema macro di volume $dx\,dy\,dz$ tale che sia in equilibrio tra t e $t+dt$

$$S = S\left(E(\vec{r},t),\ dx\,dy\,dz,\ N(\vec{r},t)\right) = S\left(E(\vec{r},t),\ N(\vec{r},t)\right)$$

$$y_i = \frac{\partial S}{\partial x_i}(\vec{r},t) \qquad \text{es. } \underbrace{T(\vec{r},t),\ P(\vec{r},t)}_{\text{campi}}$$

Ipotesi: separazione di scale di tempo e lunghezza

$$\tau_0 \ll dt \ll \tau$$

$$\xi_0 \ll dx, dy, dz \ll \xi$$

micro $\uparrow$ $\qquad$ macro $\uparrow$

Es.: $\xi_0 \sim 10^{-10}\,m$

$c \sim 100\,\frac{m}{s}$

$\tau_0 \approx \frac{\xi_0}{c} \sim 10^{-12}\,s$

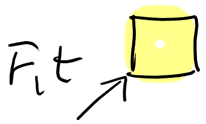
Trasporto macroscopico

Approssimazione: regime lineare

Goal: eq. del moto per $X_i(\vec{r},t)$ → $T(\vec{r},t)$, $P(\vec{r},t)$

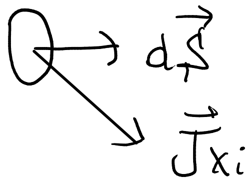
1) Densità locali → variabili estensive

$\rho_{X_i}(\vec{r},t)$ → $\rho_N(\vec{r},t)$, $\rho_E(\vec{r},t)$



$X_i(\vec{r},t)\,/\,(dx\,dy\,dz)$

2) Densità di corrente

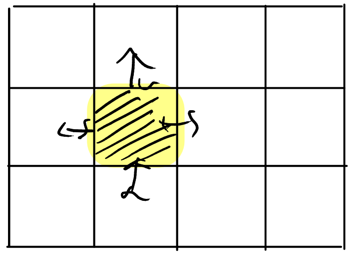


$\vec{J}_{X_i} \cdot d\vec{S} = \phi_{X_i}$ → $\vec{J}_N(\vec{r},t)$, $\vec{J}_E(\vec{r},t)$

↖ flusso di X_i

3) Equazione di continuità → conservazione di X_i

$$\frac{\partial \rho_{X_i}}{\partial t} + \vec{\nabla}\cdot\vec{J}_{X_i} = 0 \;\rightarrow\; \frac{\partial \rho_N}{\partial t} + \vec{\nabla}\cdot\vec{J}_N = 0 \,,\quad \frac{\partial \rho_E}{\partial t} + \vec{\nabla}\cdot\vec{J}_E = 0$$



4) Forze termodinamiche e correnti

variazione spaziale di Y_i $\longrightarrow$ trasporto di X_i

$\downarrow$ $\qquad\qquad$ $\downarrow$

forze termodinamiche $\qquad$ correnti

$\vec{\nabla} Y_i \Rightarrow \vec{J}_{X_i}$

5) Eq. di continuità per l'entropia

$S(\vec{r},t) \rightarrow \rho_s(\vec{r},t)$

$$\frac{\partial \rho_s}{\partial t} + \vec{\nabla}\cdot\vec{J}_s = \sigma_s$$

$\leftarrow$ tasso di produzione di entropia

$\boxed{\sigma_s \geq 0}$ II principio

Eq. locale $\rightarrow$ eq. fondamentale

$$dS = \frac{\partial S}{\partial E} dE + \frac{\partial S}{\partial V} dV + \frac{\partial S}{\partial N} dN = \frac{1}{T} dE + \cancel{\frac{P}{T} dV} - \frac{\mu}{T} dN = \frac{1}{T} dE - \frac{\mu}{T} dN$$

$$d\rho_s = \frac{1}{T} d\rho_E - \frac{\mu}{T} d\rho_N$$

a) $$\frac{\partial \rho_s}{\partial t} = \frac{1}{T}\frac{\partial \rho_E}{\partial t} - \frac{\mu}{T}\frac{\partial \rho_N}{\partial t}$$

b) $\vec{J}_S = \frac{1}{T}\vec{J}_E - \frac{\mu}{T}\vec{J}_N$

a), b) $\rightarrow$ eq. cont. $\qquad \vec{\nabla}\cdot(\phi\vec{A}) = \phi\,\vec{\nabla}\cdot\vec{A} + \vec{\nabla}\phi\cdot\vec{A}$

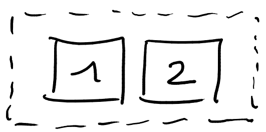
$$\frac{1}{T}\frac{\partial \rho_E}{\partial t} - \frac{\mu}{T}\frac{\partial \rho_N}{\partial t} + \vec{\nabla}\cdot\left(\frac{1}{T}\vec{J}_E\right) + \vec{\nabla}\cdot\left(-\frac{\mu}{T}\vec{J}_N\right) = \sigma_S$$

$$\frac{1}{T}\frac{\partial \rho_E}{\partial t} - \frac{\mu}{T}\frac{\partial \rho_N}{\partial t} + \frac{1}{T}\vec{\nabla}\cdot\vec{J}_E - \frac{\mu}{T}\vec{\nabla}\cdot\vec{J}_N + \vec{J}_E\cdot\vec{\nabla}\left(\frac{1}{T}\right) + \vec{J}_N\cdot\vec{\nabla}\left(-\frac{\mu}{T}\right) = \sigma_S$$

$$\sigma_S = \vec{J}_E\cdot\vec{\nabla}\left(\frac{1}{T}\right) + \vec{J}_N\cdot\vec{\nabla}\left(-\frac{\mu}{T}\right) \geq 0$$

$$\sigma_S = \sum_{i=1}^{n} \underbrace{\vec{J}_{X_i}}_{\text{corrente}}\cdot\underbrace{\vec{\nabla}Y_i}_{\text{forza termodinamica}}$$

Es.:



$V_1 = \text{cost}$
$V_2 = \text{cost}$
$E_1 + E_2 = \text{cost}$

$$dS = dS_1 + dS_2 = \frac{1}{T_1}dE_1 + \frac{1}{T_2}dE_2 = \underbrace{\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}_{\text{forza}}\underbrace{dE_1}_{\text{risposta}} \geq 0$$

Teoria di Onsager

Eq. costitutive : $\vec\nabla Y_i \leftrightarrow \vec J_{X_i}$ fenomenologiche / approssimate

Lars Onsager
Nobel 1968

$\sim$ 1800 : Fick, Fourier, Ohm

accoppiamento fenomeni irreversibili

$\sim$ 1930 : teoria di Onsager

Regime lineare :

$$\vec J_{X_i} = \sum_j L_{ij} \vec\nabla Y_j = \sum_j L_{ij} \vec F_j \qquad \vec F_i = \vec\nabla Y_i$$

coefficienti cinetici

" $L_{ij} = \dfrac{\partial J_{X_i}}{\partial F_i}$ " 1d

1) $L_{ii} > 0$ 2) $L_{ij} = L_{ji}$ relazioni di reciprocità (⚠ $\vec B$)

$$\begin{cases} \vec J_E = L_{EE} \vec\nabla\left(\frac{1}{T}\right) + L_{EN} \vec\nabla\left(-\frac{\mu}{T}\right) \\ \vec J_N = L_{NE} \vec\nabla\left(\frac{1}{T}\right) + L_{NN} \vec\nabla\left(-\frac{\mu}{T}\right) \end{cases}$$

Leggi costitutive empiriche

- **Equazione di Fick** diffusione $T = cost$

$$\vec{J}_N = - D \vec{\nabla} \rho_N$$

D = coeff. diffusione

- **Equazione di Fourier** conduzione del calore

$$\vec{J}_E = - k_T \vec{\nabla} T$$

k_T = conducibilità termica

- **Equazione di Ohm** conduzione elettrica

$$\vec{J}_e = - \sigma \vec{\nabla} \phi_e = \sigma \vec{E}$$

σ = conducibilità elettrica $\quad \vec{J}_e = \vec{J}_{Ne}$

- **Termodiffusione**

$\vec{\nabla} T \rightarrow \vec{J}_N$ effetto Ludwig-Soret

$\vec{\nabla} \rho_N \rightarrow \vec{J}_E$ effetto Dufour

- **Termoelettricità**

effetto Seebeck $\vec{\nabla} T \rightarrow \vec{E}$

effetto Peltier

Identificazione dei coefficienti di trasporto

Fick, Fourier, Ohm $\longleftrightarrow$ Teoria di Onsager

D, K_T, σ $\qquad\qquad$ L_{ij}

1) Diffusione

Fick: $\vec{J}_N = -D \vec{\nabla} \rho_N$

Onsager: $\vec{J}_N = L_{NE} \vec{\nabla}\left(\frac{1}{T}\right) + L_{NN} \vec{\nabla}\left(-\frac{\mu}{T}\right)$

$$\vec{J}_N \underset{\substack{\uparrow \\ T=\text{cost}}}{=} -\frac{L_{NN}}{T} \vec{\nabla}\mu = -\underbrace{\frac{L_{NN}}{T} \frac{\partial \mu}{\partial \rho_N}}_{D} \vec{\nabla} \rho_N \qquad D = \frac{L_{NN}}{T} \frac{\partial \mu}{\partial \rho_N}$$

es.: $\mu = \mu_0 + k_B T \ln \rho_N$ $\rightarrow$ $D = \frac{k_B L_{NN}}{\rho_N}$ $\qquad L_{NN} \sim \rho_N$ ($D = \text{cost}$)

limite diluito

2) Conduzione termica   Solido isolante

Fourier : $\vec{J}_E = -k_T \vec{\nabla} T$

Onsager : $$\begin{cases} \vec{J}_E = L_{EE} \vec{\nabla}\left(\frac{1}{T}\right) + L_{EN} \vec{\nabla}\left(-\frac{\mu}{T}\right) & 1) \\ \vec{J}_N = L_{EN} \vec{\nabla}\left(\frac{1}{T}\right) + L_{NN} \vec{\nabla}\left(-\frac{\mu}{T}\right) & 2) \end{cases}$$

$$\vec{J}_N = 0 \Rightarrow \begin{cases} \vec{J}_E = L_{EE} \vec{\nabla}\left(\frac{1}{T}\right) - \frac{L_{EN}^2}{L_{NN}} \vec{\nabla}\left(\frac{1}{T}\right) & 1)+2) \\ \vec{\nabla}\left(-\frac{\mu}{T}\right) = -\frac{L_{EN}}{L_{NN}} \vec{\nabla}\left(\frac{1}{T}\right) & 2) \end{cases}$$

$$\vec{J}_E = \frac{L_{EE}L_{NN} - L_{EN}^2}{L_{NN}} \vec{\nabla}\left(\frac{1}{T}\right) = -\underbrace{\frac{1}{T^2} \frac{L_{EE}L_{NN} - L_{EN}^2}{L_{NN}}}_{k_T} \vec{\nabla} T$$

Equazioni di trasporto

Eq. costitutive + eq. continuità $\Rightarrow$ eq. trasporto

1) Diffusione

$$\frac{\partial \rho_N}{\partial t} = -\vec{\nabla} \cdot \vec{J}_N \overset{\text{Fick}}{=} \vec{\nabla} \cdot \left(D \vec{\nabla} \rho_N \right) \overset{D = \text{cost}}{=} D \nabla^2 \rho_N$$ eq. di diffusione

2) Conduzione termica

Solido isolante

$$\frac{\partial \rho_E}{\partial t} = -\vec{\nabla} \cdot \vec{J}_E \overset{\text{Fourier}}{=} \vec{\nabla} \cdot \left(K_T \vec{\nabla} T \right) = K_T \nabla^2 T$$

$E = C_v T \qquad \rho_E = \rho c_v T$

$$\frac{\partial T}{\partial t} = \underbrace{\frac{K_T}{\rho c_v}}_{D_T} \nabla^2 T$$ eq. del calore

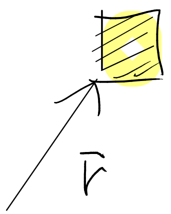
D_T = coeff. diffusione termico

Campo esterno

1) sospensione colloidale $\quad \vec{g} \rightarrow$ sedimentazione
2) conduttore elettrico $\quad \vec{E}$

$\Big\} \rightarrow T = \text{cost}$

$E, V, N, \dots$



$$\begin{cases} \phi & \text{energia potenziale per particella} \\ \Phi = N\phi & \text{energia potenziale} \end{cases} \rightarrow \begin{cases} 1) & \phi = mgz \\ 2) & \phi = e\,\Phi_e \end{cases}$$

$$S(E, N; \phi) = S(E - N\phi, N; 0)$$

pot. chimico $\quad$ pot. esterno

$$dS = \frac{1}{T}dE - \frac{\phi}{T}dN - \frac{\mu}{T}dN = \frac{1}{T}dE + \underbrace{\left(-\frac{\mu}{T} - \frac{\phi}{T}\right)}_{Y_N} dN$$

$$\vec{J}_N = L_{EN}\vec{\nabla}\left(\frac{1}{T}\right) + L_{NN}\vec{\nabla}\left(-\frac{\mu}{T} - \frac{\phi}{T}\right)$$

$T = \text{cost}$

$$= L_{EN}\underbrace{\vec{\nabla}\left(\frac{1}{T}\right)}_{=0} - \frac{L_{NN}}{T}\vec{\nabla}\mu - \frac{L_{NN}}{T}\vec{\nabla}\phi = -\frac{L_{NN}}{T}\frac{\partial \mu}{\partial \rho_N}\vec{\nabla}\rho_N - \frac{L_{NN}}{T}\vec{\nabla}\phi$$

Identificazione dei coefficienti di trasporto (campo esterno)

3) Conduzione elettrica $\qquad T = \text{cost}$

$$\vec{J}_e = \vec{J}_{N_e}\,,\quad \rho_e = \rho_{N_e}\,,\quad \phi = e\,\phi_e\,,\quad L_{ee} = L_{N_eN_e} \qquad L_{eE} = L_{N_eE}$$

Ohm : $\vec{J}_e = \sigma \vec{E} = -\sigma \vec{\nabla}\phi_e$

Onsager : $\vec{J}_e = L_{eE}\,\vec{\nabla}\left(\frac{1}{T}\right) + L_{ee}\,\vec{\nabla}\left(-\frac{\mu}{T} - \frac{\phi}{T}\right)$

$$= -\frac{L_{ee}}{T}\frac{\partial \mu}{\partial \rho_e}\vec{\nabla}\rho_e - \frac{e L_{ee}}{T}\vec{\nabla}\phi_e$$

Conduttore omogeneo : $\rho_e = \text{cost}$

$$\vec{J}_e = -\underbrace{\frac{e L_{ee}}{T}}_{\sigma}\vec{\nabla}\phi_e$$

Equazioni di trasporto (in campo esterno)

$$\begin{cases} \dfrac{\partial \rho_N}{\partial t} = - \vec{\nabla} \cdot \vec{J}_N \\ \vec{J}_N = - \dfrac{L_{NN}}{T} \dfrac{\partial \mu}{\partial \rho_N} \vec{\nabla} \rho_N - \dfrac{L_{NN}}{T} \vec{\nabla} \phi \end{cases} \qquad T = \text{cost}$$

$$\frac{\partial \rho_N}{\partial t} = \vec{\nabla} \cdot \left(\frac{L_{NN}}{T} \frac{\partial \mu}{\partial \rho_N} \vec{\nabla} \rho_N + \frac{L_{NN}}{T} \vec{\nabla} \phi \right)$$

$$= \vec{\nabla} \cdot \left(- \frac{L_{NN}}{T} \vec{F} + D \vec{\nabla} \rho_N \right) \qquad L_{NN} \sim \rho_N$$

$$\frac{\partial \rho_N}{\partial t} = \vec{\nabla} \cdot \underbrace{\Big(\underset{\substack{\uparrow \\ \text{deriva}}}{- \lambda \rho_N \vec{F}} + \underset{\substack{\uparrow \\ \text{diffusione}}}{D \vec{\nabla} \rho_N} \Big)}_{\sim \text{ Smoluchowski}} \qquad \lambda = \text{mobilità}$$

<u>Es.</u>: sistema diluito in campo esterno $\phi(\bar{r})$

in equilibrio con un bagno termico a temperatura T

Regime diluito $\rightarrow$ $\lambda \rightarrow \xi$?

$\downarrow$

$$\rho_N \sim p \sim \exp\left(-\frac{\phi(\bar{r})}{K_B T}\right)$$

$$\lambda \rho_N \vec{\nabla}\phi + D\vec{\nabla}\rho_N \sim \lambda \exp\left(-\frac{\phi}{K_B T}\right)\vec{\nabla}\phi - \frac{D}{K_B T}\vec{\nabla}\phi \exp\left(-\frac{\phi}{K_B T}\right) \sim J_N = 0$$

$$\Rightarrow \quad \lambda = \frac{D}{K_B T} \qquad D = \frac{K_B T}{\xi} \quad \Rightarrow \quad \lambda = \frac{1}{\xi}$$

EQUILIBRIO

↓

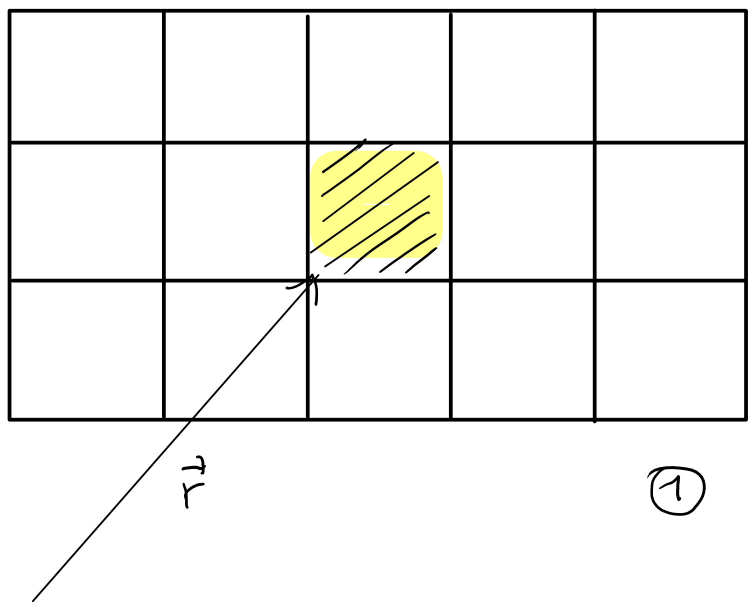
NON - EQUILIBRIO

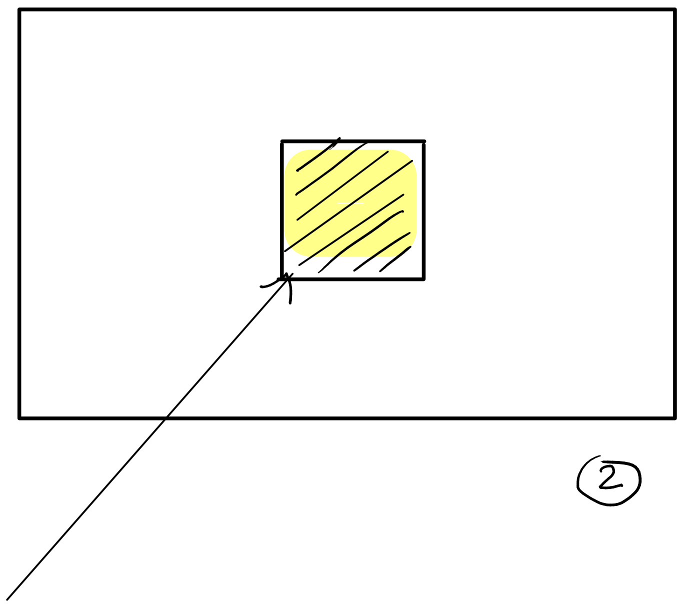
[meso] FLUTTUAZIONI TRASPORTO [macro]

statiche dinamiche

FUNZIONI DI RISPOSTA

TEORIA TERMODINAMICA DELLE FLUTTUAZIONI





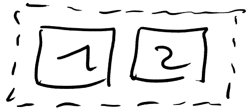
Sotto-sistemi in equilibrio locale all'interno di un sistema isolato

$\rightarrow$ statica

Sistema isolato = universo : $\{X_{u1}, \dots, X_{um}\}$ $\rightarrow$ E_u, V_u, N_u

Sottosistemi : $\{X_1, \dots, X_n\} = \{X_i\}$ $\rightarrow$ $E_1, V_1, \dots$ $\quad$ $X, \vec{X}$

<u>Esempio</u> : N_u, V_u, E_u costanti



$$\begin{cases} E_1 + E_2 = E_u \\ N_1 + N_2 = N_u \\ V_1 + V_2 = V_u \end{cases}$$

$$S_u = S_u(E_1, V_1, N_1, E_2, N_2, V_2)$$

Equilibrio: $\frac{\partial S_u}{\partial X_i} = 0 \quad \to \quad \{X_{io}\}$ equilibrio

$S(\{X_{io}\}) = S_o \quad \to \quad$ massimo

$$\frac{\partial S_u}{\partial E_1} = \frac{\partial S_1}{\partial E_1} + \frac{\partial S_2}{\partial E_1} = \frac{\partial S_1}{\partial E_1} - \frac{\partial S_2}{\partial E_2} = \frac{1}{T_1} - \frac{1}{T_2} = 0 \quad \Rightarrow \quad T_1 = T_2$$

$$\ldots \quad \Rightarrow \quad \frac{P_1}{T_1} - \frac{P_2}{T_2} = 0 \quad \Rightarrow \quad P_1 = P_2 \quad \Rightarrow$$

E_{1o}, V_{1o}, N_{1o} via eq. stato

$$\ldots \quad \Rightarrow \quad -\frac{\mu_1}{T_1} + \frac{\mu_2}{T_2} = 0 \quad \Rightarrow \quad \mu_1 = \mu_2$$

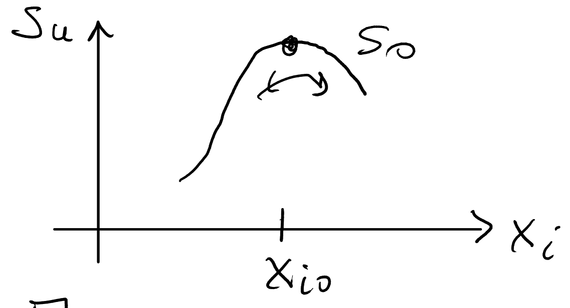
$\square$

Postulato: probabilità di una fluttuazione rispetto a $\{X_{io}\}$ è legata alla $\Delta S = S(\{X_i\}) - S_o$ da pdf $w(\{X_i\}) = w_o \exp\left[\frac{\Delta S}{k_B}\right]$

Giustificazione in fisica statistica: p = prob. microstato

$$\left.\begin{aligned} w(\{X_i\}) &= p \cdot \Omega(\{X_i\}) \\ \underbrace{w(\{X_{io}\})}_{w_o} &= p \cdot \Omega(\{X_{io}\}) \end{aligned}\right\} \quad w(\{X_i\}) = w_o \frac{\Omega(\{X_i\})}{\Omega(\{X_{io}\})}$$

$$= w_o \exp\left[(S_u(\{X_i\}) - S_o)/k_B\right] \quad \square$$



Fluttuazioni / valori medi :

$$\langle X_i \rangle = w_0 \int_{-\infty}^{\infty} dX_1 \cdots dX_n \, X_i \exp\left[\frac{\Delta S}{k_B}\right] \neq X_{i0} \to + \text{probabile}$$

$$\Delta X = X_i - \langle X_i \rangle$$

$$\langle \Delta X_i \Delta X_j \rangle = w_0 \int_{-\infty}^{\infty} dX_1 \cdots dX_n \, \Delta X_i \Delta X_j \exp\left[\frac{\Delta S}{k_B}\right] \qquad \Delta X_i \to x_i$$

Approssimazione gaussiana

$$S_u(\{X_i\}) = S_0 + \emptyset + \frac{1}{2}\sum_i \sum_j \frac{\partial^2 S_u}{\partial X_i \partial X_j} \Delta X_i \Delta X_j + O(\Delta X^3)$$

$$w(\{x_i\}) = w_0 \exp\left[\frac{1}{2k_B}\sum_i \sum_j \frac{\partial^2 S_u}{\partial X_i \partial X_j} \Delta X_i \Delta X_j\right]$$

$$K_{ij} = -\frac{\partial^2 S_u}{\partial X_i \partial X_j}$$ matrice di stabilità, simmetrica, definita positiva

$$w(\{x_i\}) = \sqrt{\frac{\det K}{(2\pi k_B)^n}} \exp\left[-\frac{1}{2k_B}\sum_i \sum_j K_{ij} \Delta X_i \Delta X_j\right]$$

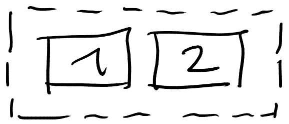
Medie e fluttuazioni

$$\langle X_i \rangle = X_{i0} \qquad (\text{gaussiana})$$

$$\langle \Delta X_i \, \Delta X_j \rangle = k_B \, K^{-1}_{ij}$$

$$\langle \Delta X_i^2 \rangle = k_B \, K^{-1}_{ii}$$

Esempio: $\{1,2\}$ isolato



N_1, N_2 cost

V_1, N_2 cost

$n=1, \; X_1 = E_1$

$E_1 + E_2 = E_u$

$T_1 = T_2 = T_u$

$$\frac{\partial^2}{\partial E_1^2} = \frac{\partial^2}{\partial E_2^2}$$

$$K_{11} = -\left.\frac{\partial^2 S_u}{\partial E_1^2}\right|_0 = -\left[\frac{\partial^2 S_1}{\partial E_1^2} + \frac{\partial^2 S_2}{\partial E_2^2}\right]$$

$$= -\left[\left.\frac{\partial}{\partial E_1}\left(\frac{1}{T_1}\right)\right|_0 + \left.\frac{\partial}{\partial E_2}\left(\frac{1}{T_2}\right)\right|_0\right]$$

$$= \left[\frac{1}{T_1^2}\left.\frac{1}{\frac{\partial E_1}{\partial T_1}}\right|_0 + \frac{1}{T_2^2}\left.\frac{1}{\frac{\partial E_2}{\partial T_2}}\right|_0\right]$$

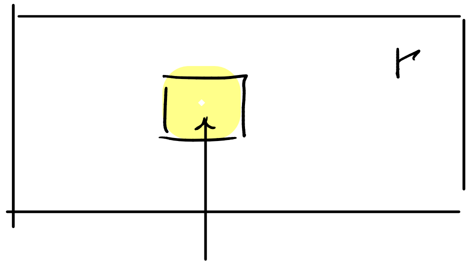
$$= \frac{1}{T_u^2}\left[\frac{1}{C_{V1}} + \frac{1}{C_{V2}}\right]$$

$$\langle \Delta E_1^2 \rangle = k_B T_u^2 \frac{1}{\frac{1}{C_{V1}} + \frac{1}{C_{V2}}}$$

$N_2 \gg N_1$

$$\longrightarrow k_B T_u^2 C_{V1} \longrightarrow \text{fis. stat: } \langle \Delta E^2 \rangle = k_B T^2 C_V$$

② Sottosistema + reservoir $(E, V, N, \ldots)$



$$S_u = S + S_r \quad \rightarrow \quad K_{ij} = -\frac{\partial S}{\partial x_i \partial x_j}$$

$$\langle \Delta x_i \Delta x_j \rangle = k_B K_{ij}^{-1}$$

Es.:

V, V_r cost

$E + E_r = E_u = \text{cost}$

$N + N_r = N_u = \text{cost}$

gran-canonico

$$\langle \Delta E^2 \rangle$$

$$\langle \Delta N^2 \rangle = k_B T V \frac{1}{\left.\frac{\partial \mu}{\partial \rho}\right|_T}$$

$$\ldots = k_B T N \rho \chi_T$$

$$\chi_T = -\frac{1}{\rho} \left.\frac{\partial \rho}{\partial P}\right|_T$$

Table 3
Complete set of fluctuation relations for a simple fluid in the μVT ensemble.

$\overline{(\Delta S)^2} = \rho_0 k c_v V + kT_0 \left(\frac{\partial\mu}{\partial\rho}\right)_T^{-1} \left(\frac{\partial\mu}{\partial T}\right)_\rho^2 V$	$\overline{\Delta\mu\,\Delta p} = \frac{kT_0}{\rho_0 v_0 V}\left(\frac{\partial\mu}{\partial\rho}\right)_T$
	$+\frac{kT_0^2}{\rho_0 c_v v_0 V}\left(\frac{\partial\mu}{\partial T}\right)_\rho \left[s_0 + \left(\frac{\partial\mu}{\partial T}\right)_\rho\right]$
$\overline{\Delta S\,\Delta N} = -kT_0 \left(\frac{\partial\mu}{\partial\rho}\right)_T^{-1} \left(\frac{\partial\mu}{\partial T}\right)_\rho V$	$\overline{\Delta S\,\Delta T} = kT_0$
$\overline{(\Delta N)^2} = kT_0 \left(\frac{\partial\mu}{\partial\rho}\right)_T^{-1} V$	$\overline{\Delta N\,\Delta\mu} = kT_0$
$\overline{(\Delta E)^2} = \rho_0 k T_0^2 c_v V$	$\overline{\Delta S\,\Delta\mu} = 0$
$+kT_0^3 \left(\frac{\partial\mu}{\partial\rho}\right)_T^{-1} \left[\left(\frac{\partial\mu}{\partial T}\right)_\rho - \frac{\mu_0}{T_0}\right]^2 V$	
$\overline{\Delta E\,\Delta S} = \rho_0 k T_0 c_v V$	$\overline{\Delta N\,\Delta T} = 0$
$-kT_0^2 \left(\frac{\partial\mu}{\partial\rho}\right)_T^{-1} \left(\frac{\partial\mu}{\partial T}\right)_\rho \left[\left(\frac{\partial\mu}{\partial T}\right)_\rho - \frac{\mu_0}{T_0}\right] V$	
$\overline{\Delta E\,\Delta N} = -kT_0^2 \left(\frac{\partial\mu}{\partial\rho}\right)_T^{-1} \left[\left(\frac{\partial\mu}{\partial T}\right)_\rho - \frac{\mu_0}{T_0}\right] V$	$\overline{\Delta S\,\Delta p} = kT_0 \frac{s_0}{v_0}$
$\overline{(\Delta T)^2} = \frac{kT_0^2}{\rho_0 c_v V}$	$\overline{\Delta E\,\Delta T} = kT_0^2$
$\overline{(\Delta\mu)^2} = \frac{kT_0}{\rho_0 V}\left[\rho_0 \left(\frac{\partial\mu}{\partial\rho}\right)_T + \frac{T_0}{c_v}\left(\frac{\partial\mu}{\partial T}\right)_\rho^2\right]$	$\overline{\Delta E\,\Delta\mu} = kT_0\mu_0$
$\overline{\Delta T\,\Delta\mu} = \frac{kT_0^2}{\rho_0 c_v V}\left(\frac{\partial\mu}{\partial T}\right)_\rho$	$\overline{\Delta E\,\Delta p} = \frac{kT_0}{v_0}(\mu_0 + T_0 s_0)$
$\overline{(\Delta p)^2} = \frac{kT_0}{v_0^2 V}\left(\frac{\partial\mu}{\partial\rho}\right)_T + \frac{kT_0^2}{\rho_0 c_v v_0^2 V}\left[s_0 + \left(\frac{\partial\mu}{\partial T}\right)_\rho\right]^2$	$\overline{\Delta N\,\Delta p} = \frac{kT_0}{v_0}$
$\overline{\Delta p\,\Delta T} = \frac{kT_0^2}{\rho_0 c_v v_0 V}\left[s_0 + \left(\frac{\partial\mu}{\partial T}\right)_\rho\right]$	

Relazione di Gibbs-Duhem:

$$N d\mu - V dP + S dT = 0$$

Variabili intensive coniugate

$$\boxed{Y_i} = \frac{\partial S}{\partial X_i} \longrightarrow \Delta Y_i = \sum_j \frac{\partial Y_i}{\partial X_j} \Delta X_j \quad \text{I Taylor}$$

forze termodinamiche

$$= \sum_j \frac{\partial^2 S}{\partial X_i \partial X_j} \Delta X_j = -\sum_j K_{ij} \Delta X_j$$

Fluttuazioni:

$$\langle \Delta X_i \Delta X_j \rangle = k_B K^{-1}_{ij}$$

$$\langle \Delta Y_i \Delta Y_j \rangle = k_B K_{ij}$$

$$\langle \Delta X_i \Delta Y_i \rangle = -k_B \delta_{ij}$$

→ fluttuazioni delle variabili estensive sono scorrelate da quelle delle variabili intensive non coniugate

The *thermodynamic forces* X_i conjugate to the fluctuations x_i are defined by

$$\Delta Y_i \leftarrow \quad X_i = \frac{\partial \Delta S}{\partial x_i} = -\sum_k g_{ik} x_k \quad \Xi_{ik} \tag{3.10}$$

ΔX_i

By analogy with Hooke's law for harmonic springs, the X_i act as 'restoring forces', tending to return the system to the thermodynamic equilibrium state of maximum entropy. In fact, as will be shown in part IV of this book, the thermodynamic forces control the entropy production during the relaxation (or regression) of spontaneous thermal fluctuations.

Statistical averages of fluctuating variables, weighted with the probability density (3.9), are easily evaluated by momentarily considering a modified distribution that produces non-zero $\langle x_i \rangle$, i.e. using the identity

$$a \int_{-\infty}^{+\infty} \mathrm{d}x_1 \ldots \int_{-\infty}^{+\infty} \mathrm{d}x_n x_i \exp\left[-\frac{1}{2k_\mathrm{B}} \sum_{i,j} g_{ij}(x_i - x_i^0)(x_j - x_j^0)\right] = x_i^0 \tag{3.11}$$

valid for any x_i^0. Differentiating both sides of this equation with respect to x_i^0, x
and then setting all the x_i^0 equal to zero, one arrives at the desired result

$$\langle x_i X_j \rangle = -\left\langle \sum_k g_{jk} x_i x_k \right\rangle = -k_\mathrm{B} \delta_{ij} \tag{3.12}$$

BH 3.2

$\underline{\text{Dim}}$: $\langle \Delta X_i \Delta Y_j \rangle = \langle \Delta X_i \left(- \sum_k \mathbb{K}_{kj} \Delta X_k \right) \rangle$

$$= a \int_{-\infty}^{\infty} dX_1 \cdots dX_n \; \Delta X_i \underbrace{\left(- \sum_k \mathbb{K}_{kj} \Delta X_k \right)}_{\frac{\partial \Delta S}{\partial \Delta X_j}} \underbrace{\exp \left[- \frac{1}{2 K_B} \sum_l \sum_m \mathbb{K}_{lm} \Delta X_l \Delta X_m \right]}_{\exp \left[\frac{\Delta S}{K_B} \right]}$$

$$= a \int_{-\infty}^{\infty} dX_1 \cdots dX_n \; \Delta X_i \left[- K_B \frac{\partial}{\partial X_j} \exp \left[\frac{\Delta S}{K_B} \right] \right]$$

$$= K_B \underbrace{a \int_{-\infty}^{\infty} dX_1 \cdots dX_n \exp \left[\frac{\Delta S}{K_B} \right]}_{=1} \underbrace{\frac{\partial \Delta X_i}{\partial \Delta X_j}}_{\delta_{ij}} = K_B \, \delta_{ij} \qquad \square$$

MACRO

Non-equilibrio

↓

Forze termodinamiche
e
correnti

↓

Coefficienti di trasporto

regime lineare
↓
Onsager

MICRO

Fluttuazioni

↓

Funzioni di correlazione dinamiche

↓

Funzioni di risposta

regime lineare
↓
teor. di fluttuaz. dissipazione

Coefficienti di trasporto → Relazioni di Green Kubo ← Funzioni di risposta

FUNZIONI DI CORRELAZIONE DIPENDENTI DAL TEMPO

$$A(\{\vec{r}(t),\vec{p}(t)\}) = A(\Gamma(t)) = A(t) \qquad \Gamma = \{\vec{r},\vec{p}\}$$

$$B(\{\vec{r}(t),\vec{p}(t)\}) = B(\Gamma(t)) = B(t)$$

Funzione di correlazione dinamica

$$C_{AB}(t',t'') = \langle A(t'')B(t')\rangle$$

Media d'ensemble

$$C_{AB}(t',t'') = \int d\Gamma(t')\, \rho(\Gamma(t'))\, A(t'')\, B(t') \qquad \Gamma(t') \longrightarrow \Gamma(t'')$$

Media temporale

$$C_{AB}(t',t'') = \lim_{T\to\infty} \frac{1}{T}\int_0^T dt_0\, A(t_0+t'')\, B(t_0+t')$$

Ipotesi di ergodicità

Equilibrio $\Rightarrow$ stazionario $\Rightarrow$ invarianza traslazione temporale

Cambio variabile : $t = t''-t'$, $s=t'$

$$C_{AB}(t) = \lim_{T\to\infty} \frac{1}{T}\int_0^T dt_0\, A(t_0+t+s)\, B(t_0+s) = \langle A(t+s)\, B(s)\rangle$$

$$C_{AB}(t) = \langle A(t)\, B(0)\rangle$$

Invarianza per inversione temporale

$$C_{AB}(t) = C_{AB}(-t) \qquad \text{pari}$$

Casi limite

$$C_{AB}(0) = \langle A(0)\, B(0)\rangle = \langle AB\rangle$$

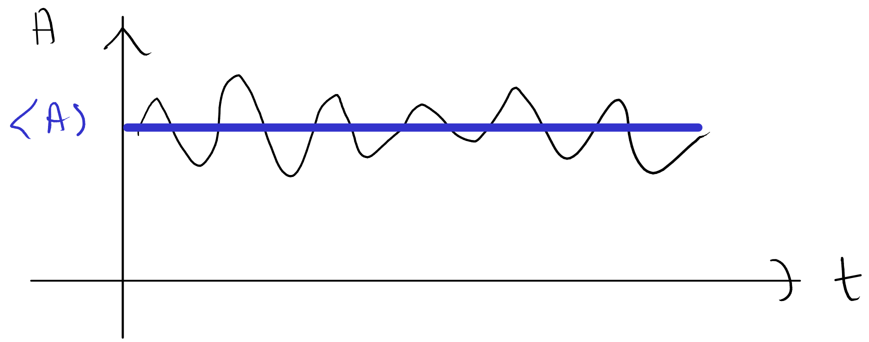
statica

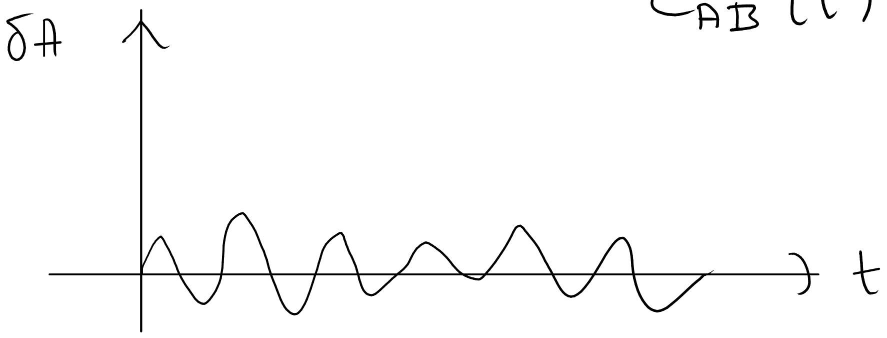
$$C_{AB}(\infty) = \langle A\rangle\langle B\rangle \quad ⚠$$

Varianti:

$$C_{AB}(t) = \langle (A(t) - \langle A\rangle)(B(t) - \langle B\rangle)\rangle = \langle \delta A(t)\, \delta B(t)\rangle$$

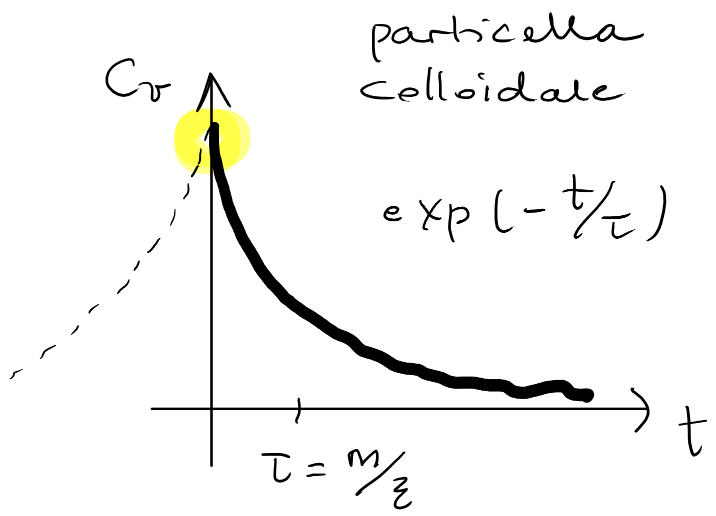
$$C_{AB}(t) = \frac{\langle A(t)\, B(0)\rangle}{\langle AB\rangle}$$

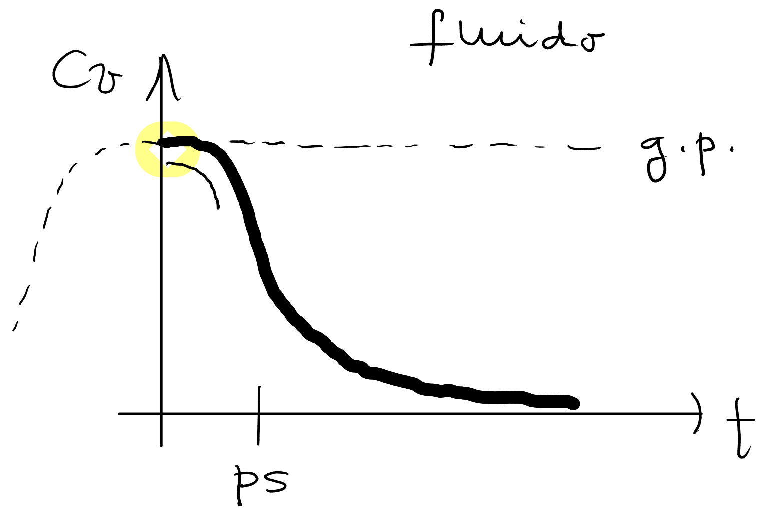


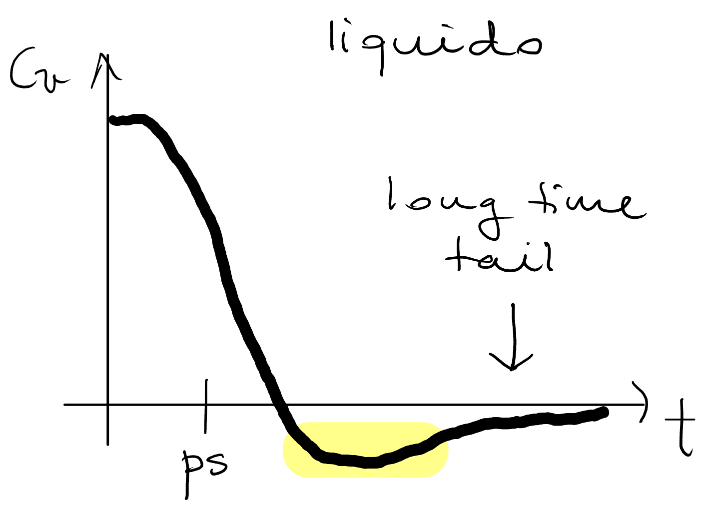


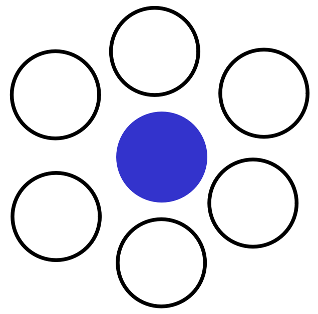
Es.: VACF f. autocorrelazione della velocità $A = B = \vec{v}$

$$C_v(t) = \frac{1}{3}\langle \vec{v}(t) \cdot \vec{v}(0) \rangle \qquad C_v(t) = \frac{1}{3N}\sum_{i=1}^{N} \langle \vec{v}_i(t) \cdot \vec{v}_i(0) \rangle$$









TEORIA DELLA RISPOSTA LINEARE

Caso statico

$H + \Delta H \qquad |\Delta H| \ll k_B T \qquad A(\{\vec{r}, \vec{p}\}) \qquad \Gamma = \{\vec{r}, \vec{p}\}$

Media in assenza di ΔH

$$\langle A \rangle = \frac{Tr[e^{-\beta H} A]}{Tr[e^{-\beta H}]} = \frac{1}{Z} Tr[e^{-\beta H} A]$$

$\Delta H \neq 0$

$$\langle A \rangle_p = \bar{A} = \frac{Tr[e^{-\beta(H+\Delta H)} A]}{Tr[e^{-\beta(H+\Delta H)}]} = \frac{Tr[e^{-\beta H}(1-\beta\Delta H) A]}{Tr[e^{-\beta H}(1-\beta\Delta H)]} + O((\beta\Delta H)^2)$$

$$= \frac{Tr[e^{-\beta H}(1-\beta\Delta H) A]}{Z[1 - \underbrace{\frac{1}{Z} Tr[e^{-\beta H}\beta\Delta H]}_{\beta\langle\Delta H\rangle}]} = (\langle A \rangle - \beta\langle \Delta H A\rangle)(1 + \beta\langle\Delta H\rangle) + O((\beta\Delta H)^2)$$

$$= \langle A \rangle - \beta \left(\langle \Delta H A \rangle - \langle \Delta H \rangle \langle A \rangle \right) + O((\beta \Delta H)^2)$$

$$\underbrace{\tilde{A} - \langle A \rangle}_{\text{risposta}} \approx -\beta \underbrace{\left(\langle \Delta H A \rangle - \langle \Delta H \rangle \langle A \rangle \right)}_{\text{fluttuazioni all'eq.}}$$

$$\Delta H = -\phi A$$

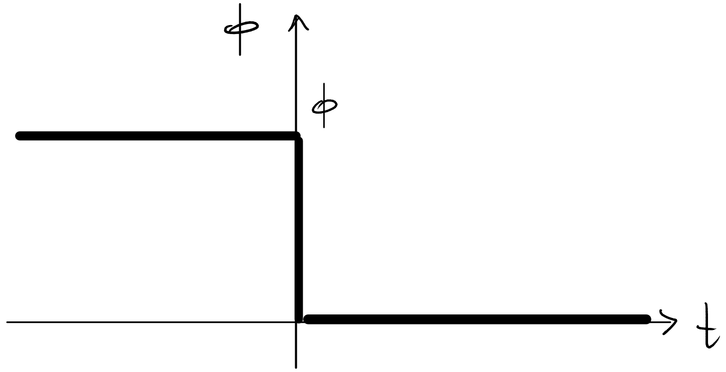
$$\delta \tilde{A} = \tilde{A} - \langle A \rangle = \beta \phi \left(\langle A^2 \rangle - \langle A \rangle^2 \right) = \beta \phi \langle \delta A^2 \rangle = \phi \, \beta \langle \delta A^2 \rangle$$

suscettibilità

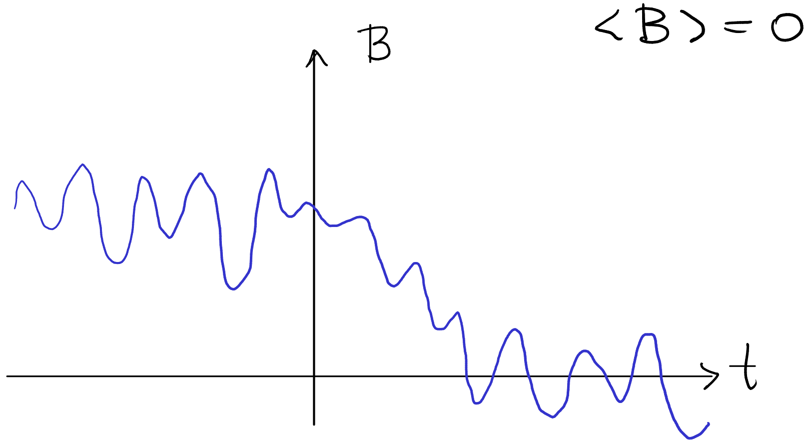
Caso dinamico

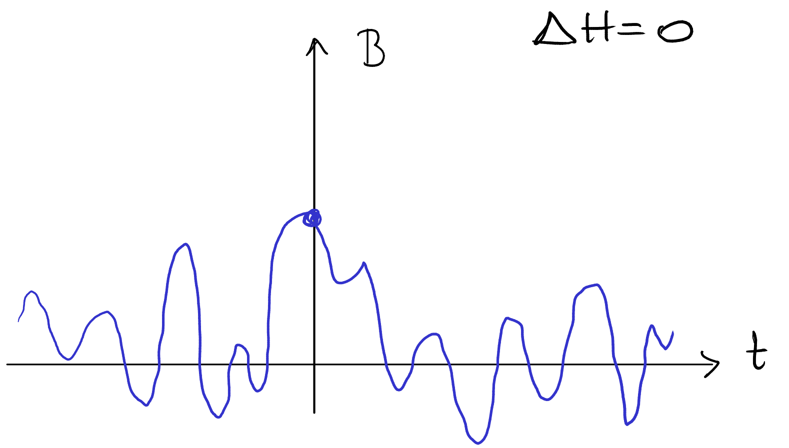
$|\Delta H| \ll k_B T \qquad \Delta H(t) \approx -\phi(t) A(t)$

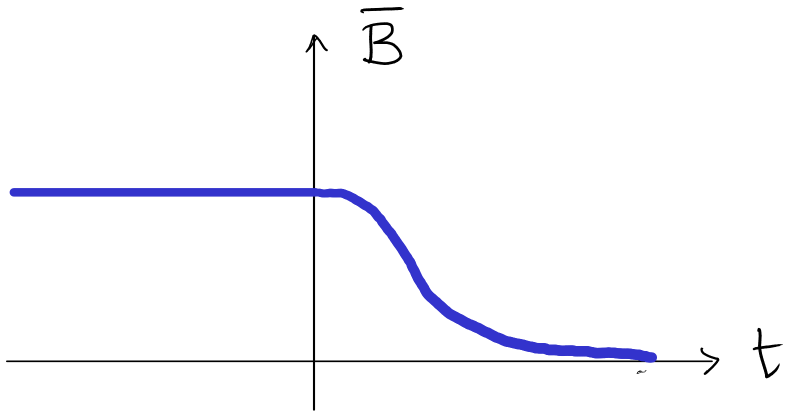
principio di regressione di Onsager



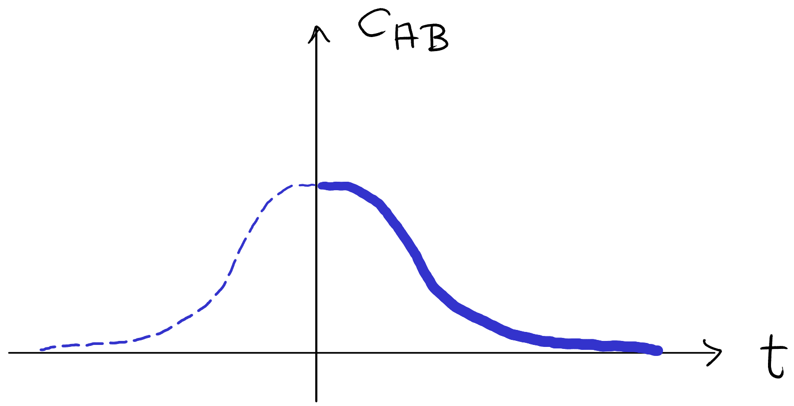
$$\phi = \begin{cases} \phi & t \leq 0 \\ 0 & t > 0 \end{cases}$$







rilassamento fuori equilibrio



fluttuazioni all'equilibrio

Per $t=0$:

$$\bar{B}(0) = \langle B(0)\rangle_p = Tr\left[e^{-\beta(H+\Delta H)} B(0) \right] / Tr\left[e^{-\beta(H+\Delta H)} \right]$$

Per $t>0$

$$\bar{B}(t) = \langle B(t)\rangle_p = Tr\left[e^{-\beta(H+\overset{-\phi A}{\Delta H})} B(t) \right] / Tr\left[e^{-\beta(H+\Delta H)} \right]$$

$$\Gamma(0) \to \Gamma(t)$$

$|\Delta H| \ll k_B T$ $\qquad$ $\Delta H = -\phi(t) A(t)$ $\qquad$ ⚠ ΔH valutato in $t=0$

$$\bar{B}(t) = \dots = \langle B\rangle - \beta\left[\langle \Delta H\, B(t)\rangle - \langle \Delta H\rangle\langle B(t)\rangle \right]$$

$$= \langle B\rangle + \beta\phi\left[\langle B(t) A(0)\rangle - \langle B\rangle\langle A\rangle \right]$$

$$\delta\bar{B}(t) = \bar{B}(t) - \langle B\rangle = \beta\phi\,\langle \delta B(t)\,\delta A(0)\rangle = \beta\phi\, C_{BA}(t) + o(\phi^2)$$

$$\delta\bar{B}(0) = \beta\phi\, C_{BA}(0)$$

Principio di regressione di Onsager

$$\frac{\delta \bar{B}(t)}{\delta \bar{B}(0)} = \frac{C_{BA}(t)}{C_{BA}(0)} \qquad t > 0$$

regime lineare

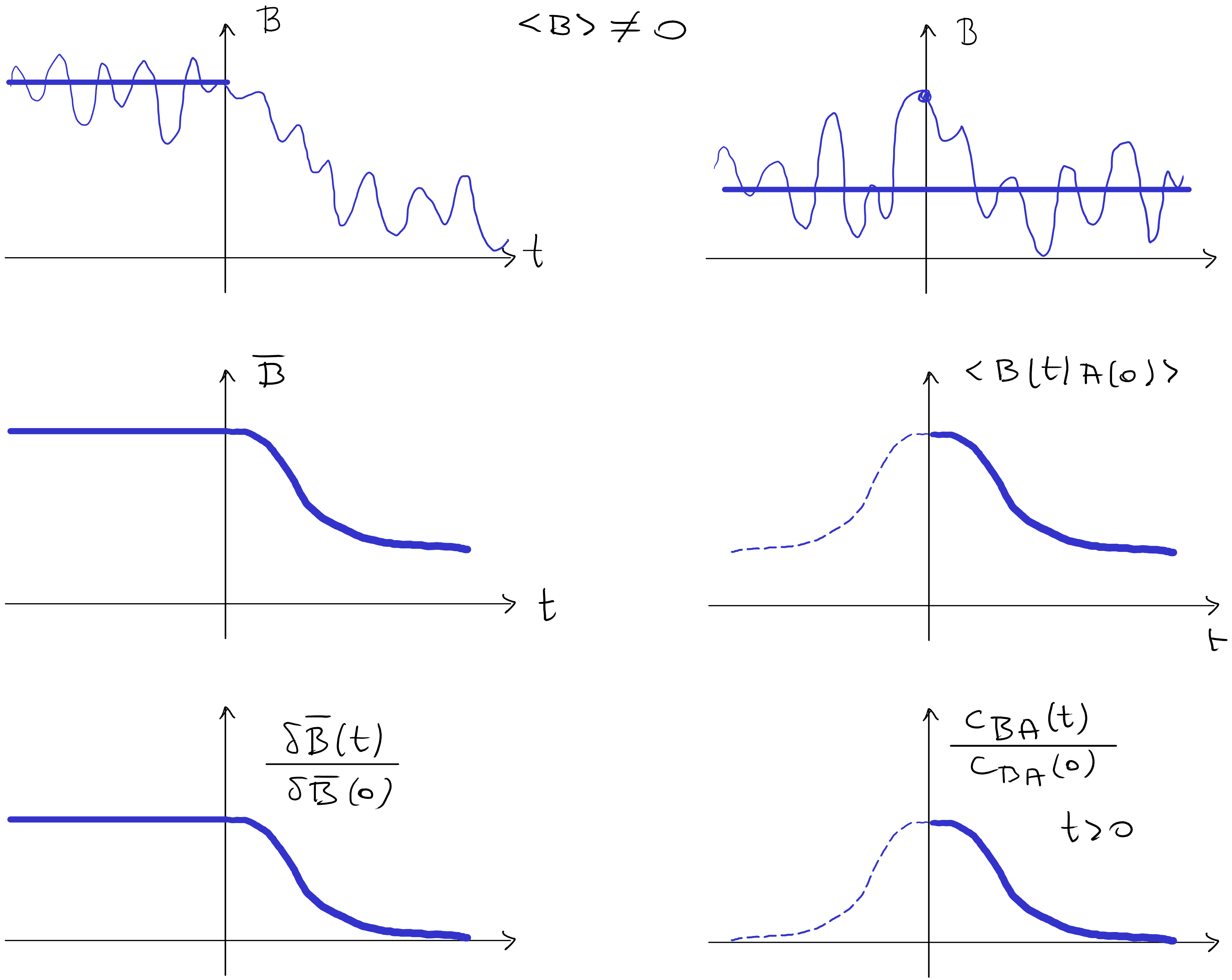
↓ evoluzione fuori eq.

↓ fluttuazioni all'eq.

tempo di correlazione

=

tempo di rilassamento



MACRO

Non-equilibrio

$\downarrow$

Forze termodinamiche e correnti

$\downarrow$

Coefficienti di trasporto $\longrightarrow$ Relazioni di Green Kubo

regime lineare $\downarrow$ Onsager

MICRO

Fluttuazioni

$\downarrow$

$\boxed{\text{Funzioni di correlazione dinamiche}}$

limite idrodinamico $\longrightarrow$ Relazioni di Green Kubo

$\downarrow$

Relazioni di Green Kubo $\longleftarrow$ Funzioni di risposta

regime lineare $\downarrow$ teor. di fluttuaz. dissipazione

Funzioni di risposta

$\delta\bar{B} = \chi\,\phi$ $\qquad\qquad$ $\Delta H = -\phi(t)\,A(t)$

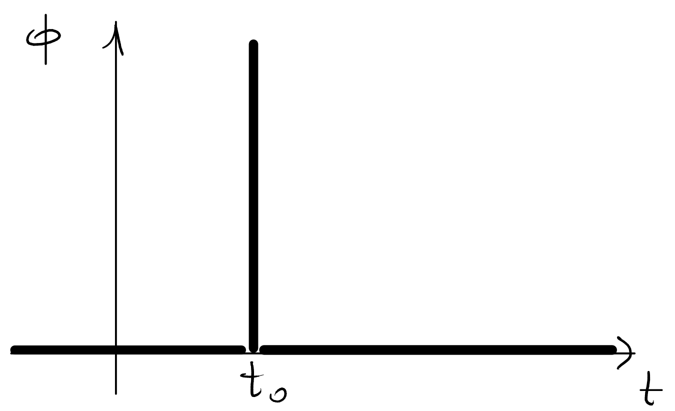
$$\delta\bar{B}(t) = \int_{-\infty}^{\infty} dt'\,\chi(t,t')\,\phi(t') \underset{\substack{\uparrow \\ \text{causalità}}}{=} \int_{-\infty}^{t} dt'\,\chi(t,t')\,\phi(t') \qquad t \geq t'$$

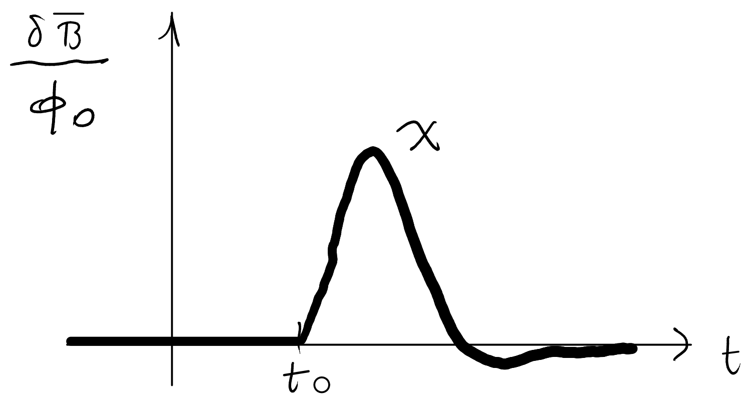
χ non dipende da ϕ (in regime lineare) $\Rightarrow$ è una proprietà all'equilibrio

$\Rightarrow$ dipende solo da $t - t' = s$

Es.: campo impulsivo $\quad \phi(t) = \phi_0\,\delta(t - t_0)$

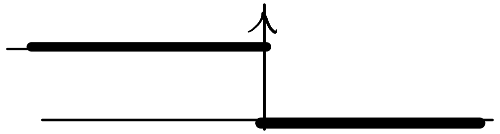
$$\delta\bar{B}(t) = \phi_0 \int_{-\infty}^{t} dt'\,\chi(t-t')\,\delta(t'-t_0) = \phi_0\,\chi(t-t_0) \Rightarrow \chi(t-t_0) = \frac{\delta\bar{B}(t)}{\phi_0}$$





Teorema di fluttuazione - dissipazione

$$\phi(t) = \begin{cases} \phi & t \leq 0 \\ 0 & t > 0 \end{cases}$$



$$s = t - t' \qquad ds = -dt'$$

$$\begin{cases} \delta \overline{B}(t) = \beta \phi \, C_{BA}(t) \\ \delta \overline{B}(t) = \int_{-\infty}^{t} dt' \, \chi_{BA}(t-t') \, \phi(t') = \phi \int_{-\infty}^{0} dt' \, \chi_{BA}(t-t') = -\phi \int_{\infty}^{t} ds \, \chi_{BA}(s) \end{cases}$$

$$\beta \, C_{BA}(t) = -\int_{\infty}^{t} ds \, \chi_{BA}(s)$$

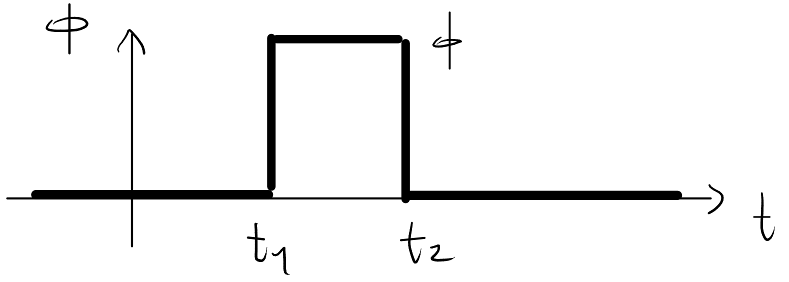
$$\beta \frac{dC_{BA}}{dt} = -\chi_{BA}(t)$$

$$\boxed{\chi_{BA}(t) = -\beta \frac{dC_{BA}}{dt}}$$

teor. fluttuazione - dissipazione $\quad \chi(t) = -\beta \dfrac{dC_A}{dt}$

Esercizio :

$\Delta H = - \phi(t) A \qquad C_{BA}(t) \simeq C_{AB}(0) \exp(-t/\tau)$

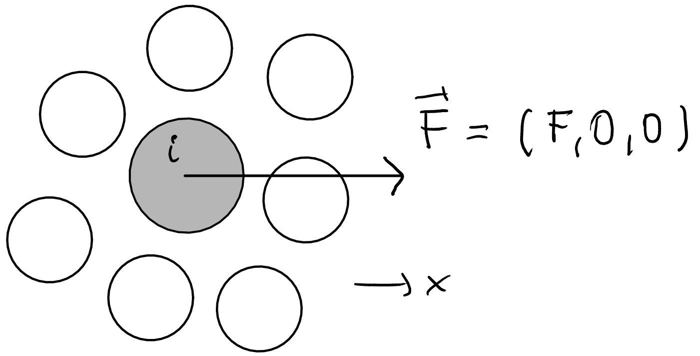


$$\phi(t) = \begin{cases} 0 & t < t_1 \\ \phi & t_1 \leq t \leq t_2 \\ 0 & t > t_2 \end{cases} \Rightarrow \begin{cases} \chi_{BA} = ? \\ \delta \overline{B}(t) = ? \end{cases}$$

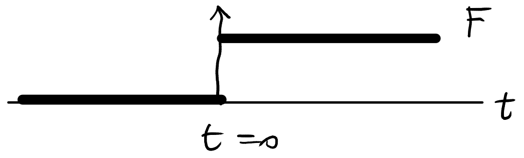
RELAZIONI DI GREEN-KUBO

Relazioni integrali tra coefficienti di trasporto e funzioni di correlazione dinamiche

1. Coefficiente di diffusione



$$\Delta H = -F x_i(t)\,\theta(t) = -\underbrace{F\theta(t)}_{\phi} \cdot \underbrace{x_i(t)}_{A}$$



$$B = v_{ix}(t) = \frac{dx_i}{dt}$$

$$\begin{cases} \delta\bar{B}(t) = \int_{-\infty}^{t} dt'\, \chi_{BA}(t-t')\,\phi(t') \\ \chi_{BA}(t) = -\beta \dfrac{dC_{BA}}{dt} \end{cases}$$

$$\frac{dC_{BA}}{dt} = \frac{d}{dt}\langle B(t+s)A(s)\rangle = \langle \frac{dB}{dt}(t+s)\,A(s)\rangle$$

$$= \langle \frac{dB}{ds}(t+s)\,A(s)\rangle = \overbrace{\frac{d}{ds}\langle B(t+s)A(s)\rangle}^{=0}$$

$$-\langle B(t+s)\frac{dA}{ds}(s)\rangle = -\langle B(t)\frac{dA}{dt}(0)\rangle$$

$$\chi_{BA}(t) = +\beta \langle B(t) \frac{dA}{dt}(0) \rangle$$

$A = x_i(t) \qquad B = v_{ix}(t) \qquad \phi(t) = F\,\theta(t) \qquad s = t - t' \quad ds = -dt'$

$$\delta \vec{v}_{ix}(t) = \beta F \int_0^t dt' \langle v_{ix}(t-t')\, v_{ix}(0) \rangle = -\beta F \int_t^0 ds \langle v_{ix}(s)\, v_{ix}(0) \rangle$$

$$= \beta F \int_0^t ds\, C_v(s) \qquad C_v = \frac{1}{3}\langle \vec{v}(t) \cdot \vec{v}(0) \rangle = \frac{1}{3N} \langle \vec{v}_i(t) \cdot \vec{v}_i(0) \rangle$$

Velocità per $t \to \infty$ = velocità di deriva

$$\delta \vec{v}_{ix}(\infty) = \beta F \int_0^\infty ds\, C_v(s)$$

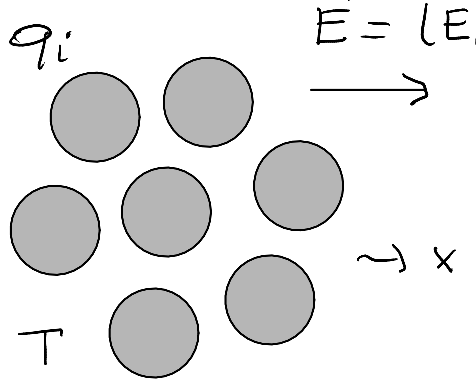
$J_{deriva} = \lambda \rho_N F = \rho_N v_{deriva} \qquad \lambda = \text{mobilità} = \frac{1}{\xi} \qquad D = \frac{K_B T}{\xi} \qquad \lambda = \frac{D}{K_B T}$

$$\lambda F = \beta F \int_0^\infty ds\, C_v(s) \Rightarrow \lambda = \beta \int_0^\infty ds\, C_v(s) \Rightarrow D = \int_0^\infty ds\, C_v(s) \qquad \underline{GK}$$

$$\langle |\Delta \vec{r}|^2 \rangle = 6t \int_0^t ds \left(1 - \frac{s}{t}\right) C_v(s) \qquad t \to \infty \quad \langle |\Delta \vec{r}|^2 \rangle \to 6 \int_0^\infty ds\, C_v(s) \cdot t = 6Dt$$

2. Conducibilità elettrica

$\vec{E} = (E, 0, 0)$



$$\Delta H = -\sum_{i=1}^{N} q_i \vec{E} \cdot \vec{r}_i(t) = -\sum_{i=1}^{N} q_i E x_i(t)$$

$$= -\underbrace{E\,\theta(t)}_{\phi} \underbrace{\sum_{i=1}^{N} q_i x_i(t)}_{A} \qquad A = \text{mom. dipolo totale}$$

$$j_{ex} = \sum_{i=1}^{N} q_i v_{ix}(t) = B$$

$$\frac{dA}{dt}(0)$$

$$\delta \bar{j}_{ex} = \boxed{\langle j_{ex} \rangle_p} - \underbrace{\langle j_{ex} \rangle}_{=0} = \beta E \int_0^t \langle j_{ex}(t-t')\, j_{ex}(0) \rangle \, dt'$$

$$\delta \bar{j}_{ex} = \beta E \int_0^t \langle j_{ex}(s)\, j_{ex}(0) \rangle \, ds$$

↳ f. autocorrelazione corrente elettrica

$$\frac{\delta \bar{j}_{ex}}{V} = \frac{\langle j_{ex} \rangle_p}{V} = \frac{\beta E}{V} \int_0^t \langle j_{ex}(s)\, j_{ex}(0) \rangle \, ds \qquad \vec{J}_e = \sigma \vec{E} \qquad J_{ex} = \sigma E$$

$$\frac{\langle j_{ex}(\infty)\rangle_P}{V} = \frac{\beta}{V}\int_0^\infty \langle j_{ex}(s)\, j_{ex}(0)\rangle \, ds \cdot E \qquad \sigma = \frac{\beta}{V}\int_0^\infty \langle j_{ex}(s)\, j_{ex}(0)\rangle \, ds \qquad \underline{GK}$$

TABLE 8.1. *Green–Kubo relations for the transport coefficients in the form of Eqn* (8.4.18)

$$K = \int_0^\infty \langle J(t)J(0)\rangle \, dt$$

K	$J(t)$	Name of current	Eqn
D	$u_{ix}(t) = \frac{d}{dt} x_i(t)$	Particle velocity	(7.2.8)
$Vk_B T\eta$	$\sigma_0^{xz}(t) = \frac{d}{dt} m \sum_{i=1}^{N} u_{ix}(t) z_i(t)$	Off-diagonal component of stress tensor	(8.4.10)
$Vk_B T(\frac{4}{3}\eta + \zeta)$	$\sigma_0^{zz}(t) - PV = \frac{d}{dt} m \sum_{i=1}^{N} u_{iz}(t) z_i(t) - PV$	Diagonal component of stress tensor	(8.5.13)
$Vk_B T^2 \lambda$	$J_0^{ez}(t) = \frac{d}{dt} \sum_{i=1}^{N} z_i(t) \left\{ \frac{1}{2} m u_i^2(t) + \frac{1}{2} \sum_{j \neq i}^{N} v[r_{ij}(t)] \right\}$	Energy current	(8.5.27)
$\left(\frac{\partial^2(\beta G/N)}{\partial c^2}\right)_{P,T} D_{12}$	$j_x^c(t) = \frac{d}{dt} \left\{ (1-c) \sum_{i=1}^{N_1} x_{i1}(t) - c \sum_{i=1}^{N_2} x_{i2}(t) \right\}$	Interdiffusion current	(8.6.31)
$Vk_B T\sigma$	$j_x^Z(t) = \frac{d}{dt} \sum_{i=1}^{N} q_i x_i(t)$	Electrical current	(7.8.10)

Note: $c = N_1/(N_1 + N_2)$; q_i is the charge carried by particle i.

Hansen MacDonald

FUNZIONI DI CORRELAZIONE DIPENDENTI DALLO SPAZIO E DAL TEMPO

2 punti nel tempo t', t''

2 punti nello spazio $\bar{r}', \bar{r}''$

→ tempo
→ spazio-tempo
} dinamiche

→ spazio → statiche

spazio reale $\bar{r}$	tempo t
spazio reciproco $\vec{k}$	frequenze ω

Osservabili statiche

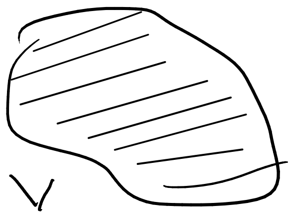
$\{ \bar r_i \} \quad i = 1, \dots, N$

$$\hat A(\vec r) = \sum_{i=1}^{N} a_i \, \delta(\bar r - \bar r_i)$$

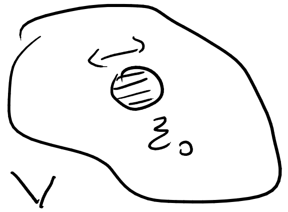
Es.: densità microscopica $\quad a_i = 1$

$$\hat \rho(\vec r) = \sum_{i=1}^{N} \delta(\bar r - \bar r_i)$$

Integro su tutto il volume



$$\int_V \hat\rho(\vec r)\, d\vec r = N$$



$$\int_{\xi_0^3} \hat\rho(\vec r)\, d\vec r = \begin{cases} 0 \\ 1 \end{cases}$$

Media d'ensemble

$$\langle \hat\rho(\bar r) \rangle = \underset{\uparrow}{\rho(\vec r)} \neq \rho_N(\vec r)$$

densità locale

Sistema omogeneo

$$\rho(\vec r) = \rho = \frac{N}{V} \quad \to \quad \langle \hat\rho(\bar r')\, \hat\rho(\bar r'') \rangle$$

Osservabili dinamiche

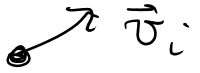
$$\hat{A}(\vec r,t) = \sum_{i=1}^{N} a_i(t)\,\delta(\vec r - \vec r_i(t)) \qquad \hat{A}_{k} = \int d\vec r\, e^{-i\vec k\cdot\vec r}\,\hat{A}(\vec r) = \sum_{i=1}^{N} a_i(t)\, e^{-i\vec k\cdot\vec r_i(t)}$$

Es.: densità micro

$$\hat{\rho}(\vec r,t) = \sum_{i=1}^{N} \delta(\vec r - \vec r_i(t)) \qquad \hat{\rho}_{\vec k}(t) = \sum_{i=1}^{N} e^{-i\vec k\cdot\vec r_i(t)}$$

Es.: corrente micro $\quad a_i = v_i$

$$\hat{j}(\vec r,t) = \sum_{i=1}^{N} \vec v_i\,\delta(\vec r - \vec r_i(t))$$



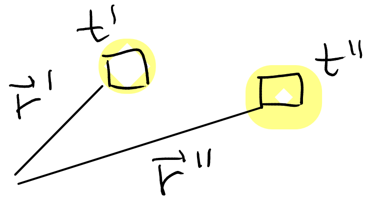
Proprietà di simmetria

$$C_{AB}(\vec{r}',\vec{r}'',t',t'') = \langle \hat{A}(\vec{r}',t')\,\hat{B}(\vec{r}'',t'')\rangle$$

$$C_{AB}(\vec{k}',\vec{k}'',t',t'') = \langle \hat{A}_{\vec{k}'}(t')\,\hat{B}^{*}_{\vec{k}''}(t'')\rangle = \langle \hat{A}_{\vec{k}'}(t')\,\hat{B}_{-\vec{k}''}(t'')\rangle$$

- Stazionarietà : $t = t'' - t'$
- Omogeneità : $\vec{r} = \vec{r}'' - \vec{r}'$ $\qquad \vec{k} = \vec{k}' = \vec{k}''$
- + Isotropia : $|\vec{r}| = |\vec{r}'' - \vec{r}'|$ $\qquad |\vec{k}| = |\vec{k}'| = |\vec{k}''|$

FUNZIONI DI CORRELAZIONE DELLA DENSITÀ MICROSCOPICA : SPAZIO REALE



$$\hat{\rho}(\vec{r},t) = \sum_{i=1}^{N} \delta(\vec{r} - \vec{r}_i(t)) \qquad \langle \hat{\rho}(\vec{r}) \rangle = \rho(\vec{r})$$

Caso statico :

$$\hat{\rho}(\vec{r}) = \sum_{i=1}^{N} \delta(\vec{r} - \vec{r}_i)$$

$$G(\vec{r}', \vec{r}'') = \langle (\hat{\rho}(\vec{r}') - \rho(\vec{r}'))(\hat{\rho}(\vec{r}'') - \rho(\vec{r}'')) \rangle$$

omogeneo : $\rho(\vec{r}) = \rho$

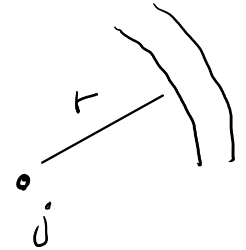
$$= \langle \hat{\rho}(\vec{r}')\hat{\rho}(\vec{r}'') \rangle - \rho^2 \qquad \vec{r} = \vec{r}'' - \vec{r}'$$

$$G(\vec{r}) = \frac{1}{N}\int_V d\vec{r}' \langle \hat{\rho}(\vec{r}')\hat{\rho}(\vec{r}'+\vec{r}) \rangle - \frac{V}{N}\rho^2 = \frac{1}{N}\int_V d\vec{r}' \langle \hat{\rho}(\vec{r}')\hat{\rho}(\vec{r}'+\vec{r}) \rangle - \rho$$

$$= \frac{1}{N}\int_V d\vec{r}' \langle \sum_{i=1}^{N}\sum_{j=1}^{N} \delta(\vec{r}' - \vec{r}_j)\,\delta(\vec{r}' + \vec{r} - \vec{r}_i) \rangle - \rho$$

$$= \frac{1}{N} \langle \sum_{i=1}^{N}\sum_{j=1}^{N} \delta(\vec{r} - (\vec{r}_i - \vec{r}_j)) \rangle - \rho = G_s(\vec{r}) + G_d(\vec{r}) - \rho$$

$$= \delta(\vec r) + \frac{1}{N}\left\langle \sum_{i=1}^{N} \sum_{j=1}^{N}{}' \delta(\vec r - (\vec r_i - \vec r_j)) \right\rangle - \rho$$



Funzione di distribuzione di coppia (o radiale): $g(\vec r)$

$$g(\vec r) = \frac{1}{\rho N}\left\langle \sum_{i=1}^{N} \sum_{j=1}^{N}{}' \delta(\vec r - (\vec r_i - \vec r_j)) \right\rangle = \frac{G_d(\vec r)}{\rho}$$

$$G(\vec r) = \delta(\vec r) + \rho\, g(\vec r) - \rho = \rho\,[\underbrace{g(\vec r) - 1}_{h(\vec r)}] + \delta(\vec r)$$

isotropo $g(r)$

f. distribuzione parziali $g_{\alpha\beta}(r)$

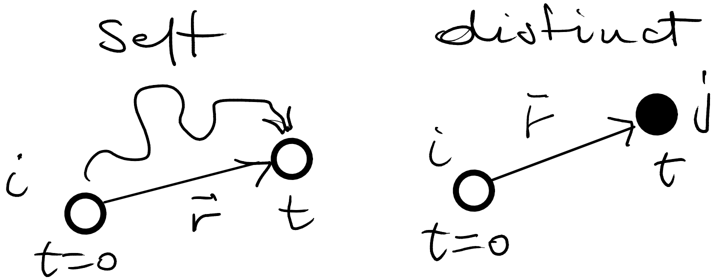
$\alpha,\beta = A, B, \dots$

Caso dinamico:

$$\hat\rho(\vec r, t) = \sum_{i=1}^{N} \delta(\vec r - \vec r_i(t))$$ sistema stazionario, omogeneo

$$G(\vec r, t) = \frac{1}{N}\int_V d\vec r' \left\langle (\hat\rho(\vec r', 0) - \rho)(\hat\rho(\vec r' + \vec r, t) - \rho) \right\rangle$$

van Hove



$$= \frac{1}{N}\int_V d\vec r' \left\langle \hat\rho(\vec r', 0)\, \hat\rho(\vec r' + \vec r, t) \right\rangle - \rho = \dots =$$

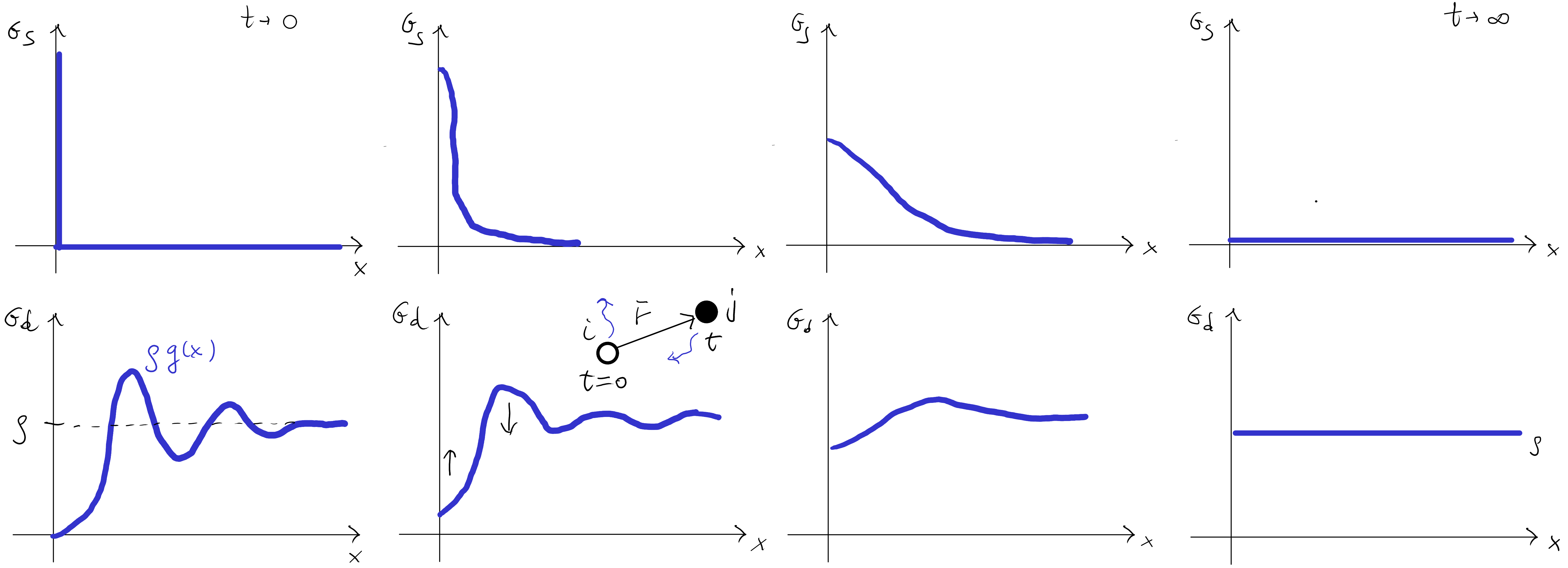
$$= \frac{1}{N}\left\langle \sum_{i=1}^{N} \sum_{j=1}^{N} \delta(\vec r - (\vec r_i(t) - \vec r_j(0))) \right\rangle - \rho = G_s(\vec r, t) + G_d(\vec r, t) - \rho$$

$$= \frac{1}{N}\sum_{i=1}^{N} \left\langle \delta(\vec r - (\vec r_i(t) - \vec r_i(0))) \right\rangle + \frac{1}{N}\sum_{i=1}^{N}\sum_{j=1}^{N}{}' \left\langle \delta(\vec r - (\vec r_i(t) - \vec r_j(0))) \right\rangle - \rho$$

Casi limite

$$\lim_{t\to 0} G_s(\vec r, t) = \delta(\vec r) \qquad \int_V d\vec r\, G_s(\vec r, t) = 1 \qquad \lim_{t\to\infty} G_s(\vec r, t) = \frac{1}{V} \approx 0$$

$$\lim_{t\to 0} G_d(\vec r, t) = \rho\, g(\vec r) \qquad \int_V d\vec r\, G_d(\vec r, t) = N-1 \qquad \lim_{t\to\infty} G_d(\vec r, t) = \frac{N-1}{V} \approx \rho$$



FUNZIONI DI CORRELAZIONE DELLA DENSITÀ MICROSCOPICA: SPAZIO DI FOURIER

$$\hat{\rho}_{\vec{k}}(t) = \int d\vec{r}\, e^{-i\vec{k}\cdot\vec{r}}\, \hat{\rho}(\vec{r},t) = \sum_{i=1}^{N} e^{-i\vec{k}\cdot\vec{r}_i(t)}$$ stazionario, omogeneo

caso statico

$$S(\vec{k}) = \frac{1}{N}\langle \hat{\rho}_{\vec{k}}\, \hat{\rho}_{-\vec{k}} \rangle \qquad \left(= \frac{1}{N}\langle \delta\hat{\rho}_{\vec{k}}\, \delta\hat{\rho}_{-\vec{k}} \rangle \right)$$ Fattore di struttura

$$= \frac{1}{N}\int d\vec{r}''\, e^{-i\vec{k}\cdot\vec{r}''}\int d\vec{r}'\, e^{i\vec{k}\cdot\vec{r}'} \langle \hat{\rho}(\vec{r}')\,\hat{\rho}(\vec{r}'')\rangle \qquad \vec{r} = \vec{r}'' - \vec{r}'$$

$$= \frac{1}{N}\int d\vec{r}'\int d\vec{r}\, e^{-i\vec{k}\cdot\vec{r}} \langle \hat{\rho}(\vec{r}')\,\hat{\rho}(\vec{r}'+\vec{r})\rangle$$

$$= \int d\vec{r}\, e^{-i\vec{k}\cdot\vec{r}}\, \underbrace{\frac{1}{N}\int d\vec{r}' \langle \hat{\rho}(\vec{r}')\,\hat{\rho}(\vec{r}'+\vec{r})\rangle}_{G(\vec{r})+\rho} = \int d\vec{r}\, e^{-i\vec{k}\cdot\vec{r}}\, G(\vec{r}) + \rho\,\delta(\vec{k})$$

$$G(\vec{r}) = \rho\,[g(\vec{r})-1] + \delta(\vec{r})$$

$$\rho\int d\vec{r}\, e^{-i\vec{k}\cdot\vec{r}}\,(g(\vec{r})-1)$$

$$= \rho\int d\vec{r}\, e^{-i\vec{k}\cdot\vec{r}}\,[g(\vec{r})-1] + 1 + \rho\,\delta(\vec{k}) = 1 + \rho\, h(\vec{k}) + \rho\,\delta(\vec{k})$$

$$S(\vec{k}) = \frac{1}{N}\langle \hat{\rho}_{\vec{k}}\,\hat{\rho}_{-\vec{k}}\rangle = \frac{1}{N}\left\langle \sum_{i=1}^{N} e^{-i\vec{k}\cdot\vec{r}_i} \cdot \sum_{j=1}^{N} e^{i\vec{k}\cdot\vec{r}_j}\right\rangle = \frac{1}{N}\left\langle \sum_{i=1}^{N}\sum_{j=1}^{N} e^{-i\vec{k}\cdot(\vec{r}_i-\vec{r}_j)}\right\rangle$$

isotropo: $S(k)$ $\quad |\vec{k}| = k \quad k_0 = \frac{2\pi}{L} \quad (n, m, l)\cdot\frac{2\pi}{L} = \vec{k}$ PBC

primo picco: $k_* \approx \frac{2\pi}{\varepsilon_0}$ $\quad$ O-O

$$\lim_{k\to 0} S(k) = \rho\, k_B T\, \chi_T$$ $\to$ compressibilità isoterma

Caso dinamico

$$F(\vec{k},t) = \frac{1}{N}\langle \hat{\rho}_{\vec{k}}(t)\,\hat{\rho}_{-\vec{k}}(0)\rangle$$ f. intermedia di scattering totale

$$= \int d\vec{r}\, e^{-i\vec{k}\cdot\vec{r}}\left[G(\vec{r},t) + \rho\right]$$ van Hove: $G(\vec{r},t)$

$$= \int d\vec{r}\, e^{-i\vec{k}\cdot\vec{r}}\, G(\vec{r},t) + \rho\,\delta(\vec{k})$$ $\quad G(\vec{r},t) = G_s + G_d$

$$F_s(\vec{k},t) = \int d\vec{r}\, e^{-i\vec{k}\cdot\vec{r}}\, G_s(\vec{r},t) = \frac{1}{N}\left\langle \sum_{i=1}^{N} \exp\left[-i\vec{k}\cdot(\vec{r}_i(t) - \vec{r}_i(0))\right]\right\rangle$$ self

$$\lim_{t\to 0} F(\vec{k},t) = S(\vec{k}) \qquad \lim_{t\to\infty} F(\vec{k},t) = \lim_{t\to\infty} F_s(\vec{k},t) = 0$$

REGIMI DINAMICI

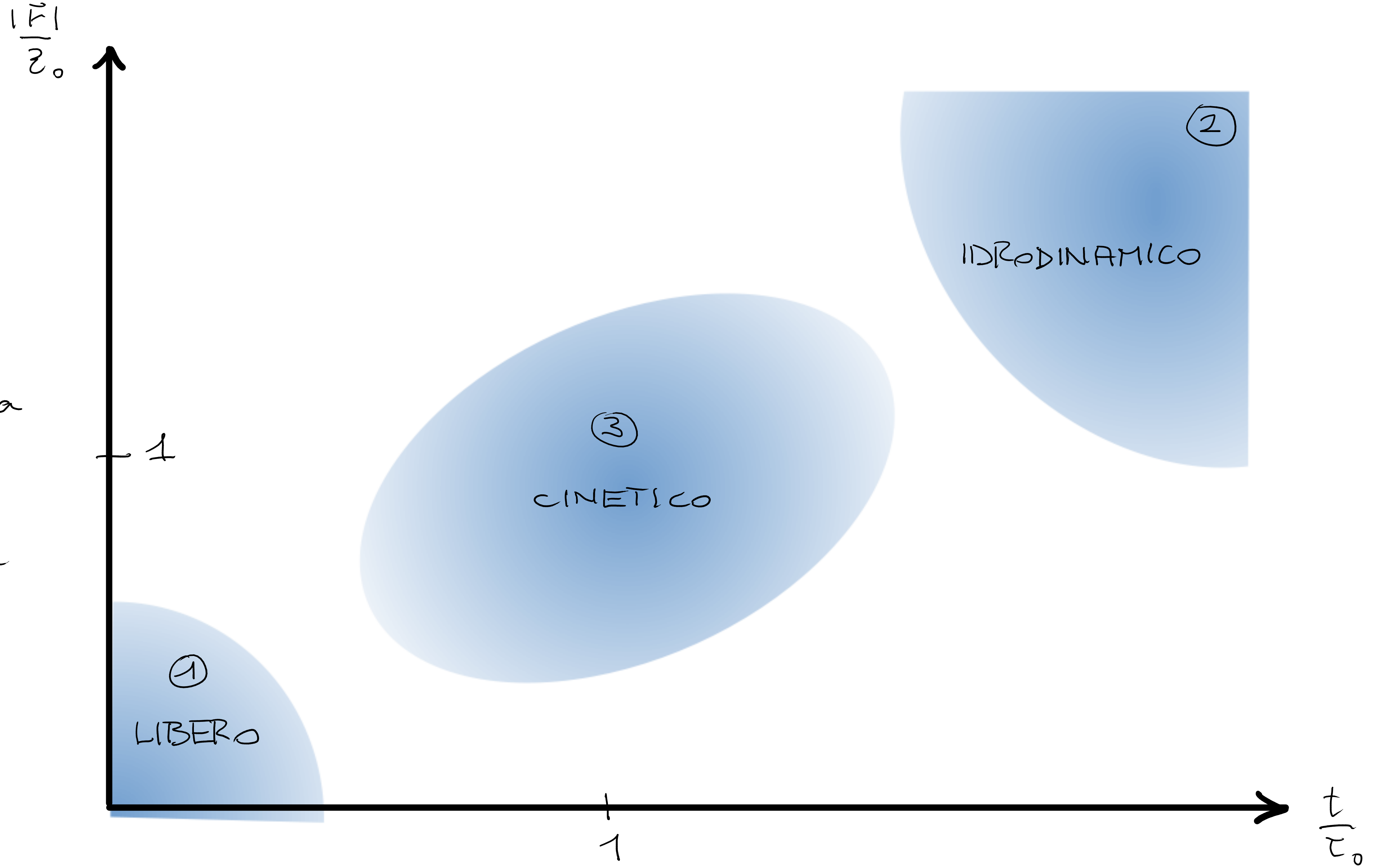
$G(\vec{r},t)$ van Hove

$F(\vec{k},t)$ intermedia di scattering

$S(\vec{k},\omega)$ fattore di struttura dinamico

r_0 distanza interatomica tipica

τ_0 tempo microscopico



① Regime libero

$|\vec{r}| \ll \xi_0 \qquad t \ll \tau_0 \qquad |\vec{k}|\,\xi_0 \gg 1$

$\vec{v}\,t \qquad \vec{r} = \vec{v}\,t$

Gas perfetto equilibrio a temperatura T

$$\begin{cases} G_d(\vec{r},t) = \rho \\ G_s(\vec{r},t) \sim p_{MB}\left(\vec{v} = \dfrac{\vec{r}}{t}\right) \end{cases}$$

$$G(\vec{r},t) = G_s(\vec{r},t) + G_d(\vec{r},t) - \rho$$

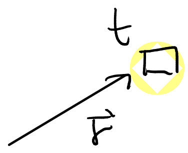
$$= \left(\frac{m}{2\pi k_B T t^2}\right)^{3/2} \exp\left(-\frac{m}{2 k_B T t^2}\,|\vec{r}|^2\right)$$

$$F_s(\vec{k},t) = \exp\left(-\frac{2 k_B T\,|\vec{k}|^2}{m}\,t^2\right) = F(\vec{k},t)$$

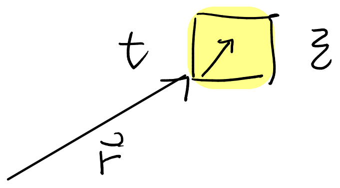
2) Regime idrodinamico

$|\vec r| \gg \xi_0 \qquad t \gg \tau_0 \qquad |\vec k|\,\xi_0 \ll 1$

$$\hat\rho(\vec r,t) = \sum_{i=1}^{N} \delta(\vec r - \vec r_i(t)) \qquad\qquad \rho_N(\vec r,t)$$



$$\langle \hat\rho(\vec r,t)\rangle = \rho(\vec r,t) \qquad\qquad \rho_N(\vec r,t) = \frac{1}{\xi^3}\int_{\xi^3} d\vec r\,'\,\hat\rho(\vec r+\vec r\,',t)$$



$$\hat\rho_{\vec k}(t) \to \rho_{\vec k}(t) \qquad\qquad \rho_{N,\vec k}(t)$$

BH 11.5

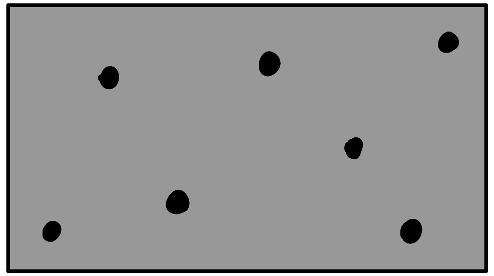
$G(\vec r,t)$

$F(\vec k,t)$

$$\langle \hat\rho_{\vec k}(t)\,\hat\rho_{-\vec k}(0)\rangle = \langle \rho_{N,\vec k}(t)\,\rho_{N,-\vec k}(0)\rangle \to \text{Onsager}$$

N_0 tagged particles

$$F_s(\vec k,t) = \frac{1}{N_0}\langle \hat\rho_{\vec k}(t)\,\hat\rho_{-\vec k}(0)\rangle = \frac{1}{N_0}\langle \rho_{N,\vec k}(t)\,\rho_{N,-\vec k}(0)\rangle$$



$$\frac{\partial \rho_N}{\partial t} = D\,\nabla^2 \rho_N \qquad \frac{\partial \rho_{N,\vec k}}{\partial t} = -Dk^2\,\rho_{N,\vec k} \qquad \rho_{N,\vec k}(t) = \rho_{N,\vec k}(0)\,e^{-Dk^2 t}$$

$$F_S(\vec{k},t) = \underbrace{\frac{\langle \rho_{N,\vec{k}}(0)\, \rho_{N,-\vec{k}}(0) \rangle}{N_0}}_{=1} \exp(-Dk^2t) = \exp(-Dk^2t)$$

$$G_S(\vec{r},t) = \frac{1}{(4\pi Dt)^{3/2}} \exp\left(-\frac{1}{4Dt}|\vec{r}|^2\right)$$

3) Regime cinetico $\quad |\vec{r}| \sim \xi_0 \quad t \sim \tau_0 \quad |\vec{k}|\xi_0 \sim 1$

a) Approssimazione gaussiana

$$G_s(\vec{r},t) = \left(\frac{\alpha(t)}{\pi}\right)^{3/2} \exp\left(-\alpha(t)\,|\vec{r}|^2\right)$$

α dipende solo da t

regime libero : $\alpha(t) = \dfrac{m}{2 k_B T\, t^2}$

regime idro : $\alpha(t) = \dfrac{1}{4Dt}$

$$\langle|\Delta\vec{r}(t)|^2\rangle = \frac{1}{N}\sum_{i=1}^{N} \langle \underbrace{|\vec{r}_i(t) - \vec{r}_i(0)|}_{|\vec{r}|}{}^2 \rangle = \int d\vec{r}\, |\vec{r}|^2 G_s(\vec{r},t)$$

isotropo

$$= 3\int_{-\infty}^{\infty} dx\, x^2 G_s(x,t) = 3\int_{-\infty}^{\infty} dx\, x^2 \left(\frac{\alpha(t)}{\pi}\right)^{3/2} \exp\left(-\alpha(t)\,x^2\right)$$

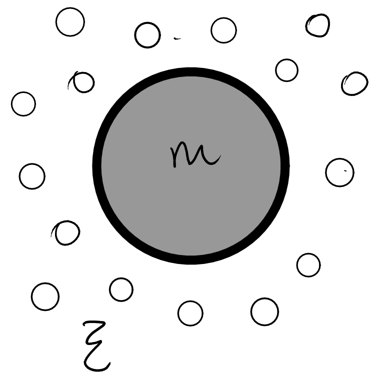
$$= 3\cdot\frac{1}{2\alpha(t)} = \frac{3}{2}\,\frac{1}{\alpha(t)} \qquad \boxed{\alpha(t) = \frac{3}{2\langle|\Delta\vec{r}(t)|^2\rangle}}$$

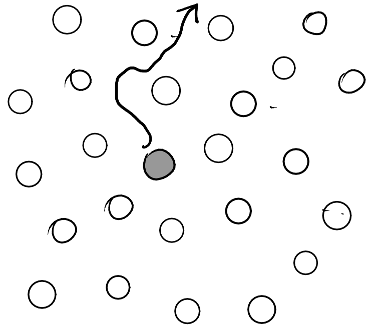
$\to \alpha_2(t)$

non-gaussianità

$$F_s(\vec{k},t) = \exp\left(-\frac{1}{4\alpha(t)}\,|\vec{k}|^2\right) = \exp\left(-\frac{1}{6}\,|\vec{k}|^2 \langle|\Delta\vec{r}(t)|^2\rangle\right)$$

b) Funzioni di memoria





Langevin : $m \frac{d\vec{v}}{dt} = -\xi \vec{v} + \vec{\theta}(t)$

$\langle \vec{\theta}(t) \rangle = \vec{0}$

$\langle \theta_\alpha(t') \theta_\beta(t'') \rangle = 2\theta_0 \delta_{\alpha\beta} \delta(t'-t'')$

Eq. Langevin generalizzata $\quad \xi \to M(t) \quad t' < t$

$$m \frac{d\vec{v}}{dt} = - \int_{-\infty}^{t} dt' \, M(t-t') \, \vec{v}(t') + \vec{\theta}(t) \qquad \langle \vec{\theta}(t) \rangle = \vec{0} \qquad \langle \vec{v}(0) \cdot \vec{\theta}(t) \rangle \underset{\downarrow}{\overset{t>0}{}} = \vec{0}$$

Operatore di proiezione di Mori - Zwanzig

$$\left\langle \frac{d\vec{v}}{dt} \cdot \vec{v}(0) \right\rangle = - \frac{1}{m} \int_{-\infty}^{t} dt' \, M(t-t') \, \langle \vec{v}(t') \cdot \vec{v}(0) \rangle + \overbrace{\langle \vec{\theta}(t) \cdot \vec{v}(0) \rangle}^{= \vec{0}}$$

$$\frac{dC_v}{dt} = - \frac{1}{m} \int_{-\infty}^{t} dt' \, M(t-t') \, C_v(t')$$

- Memoria esponenziale

$$M(t) = M(0) \exp(-t/\tau)$$

$$C_v(t) = \frac{k_B T}{m(\alpha_+ - \alpha_-)} \left(\alpha_+ e^{-\alpha_- |t|} - \alpha_- e^{-\alpha_+ |t|} \right)$$

$$\alpha_\pm = \frac{1}{2\tau} \left[1 \mp \left(1 - 4 \Omega_0^2 \tau^2 \right)^{1/2} \right]$$

$\tau < \frac{1}{2\Omega_0}$: α_-, α_+ reali $\nearrow T$

$\tau > \frac{1}{2\Omega_0}$: α_-, α_+ imm. $\searrow T$

$$C_v(t) \simeq 1 - \frac{1}{2} \Omega_0^2 t^2 + O(t^4)$$

$$\downarrow$$

$$\langle |\vec{F}|^2 \rangle$$

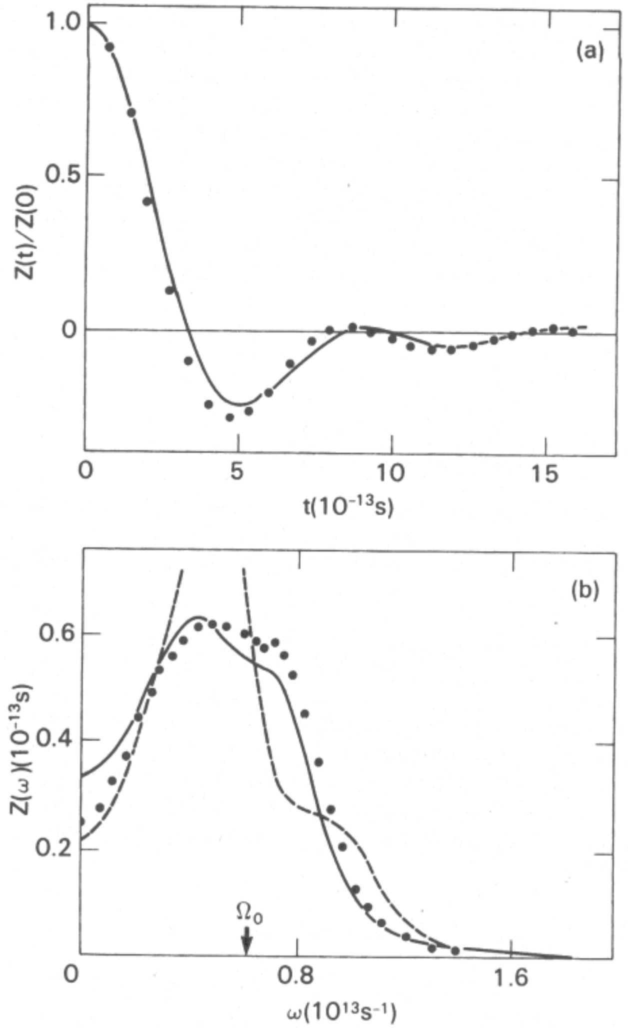


FIG. 9.5. Velocity autocorrelation function (a) and the associated power spectrum (b) of a model of liquid rubidium. The points are molecular dynamics results (Rahman, 1974b), the full curves correspond to the theory of Gaskell and Miller (1978a) (see Eqn (9.5.9)) and the dashed curve in (b) is calculated from the theory of Bosse *et al.* (1978d) (see Eqns (9.5.16)). The low-frequency peak in $Z(\omega)$ arises from the coupling to the transverse current and the shoulder at higher frequencies comes from the coupling to the longitudinal current.

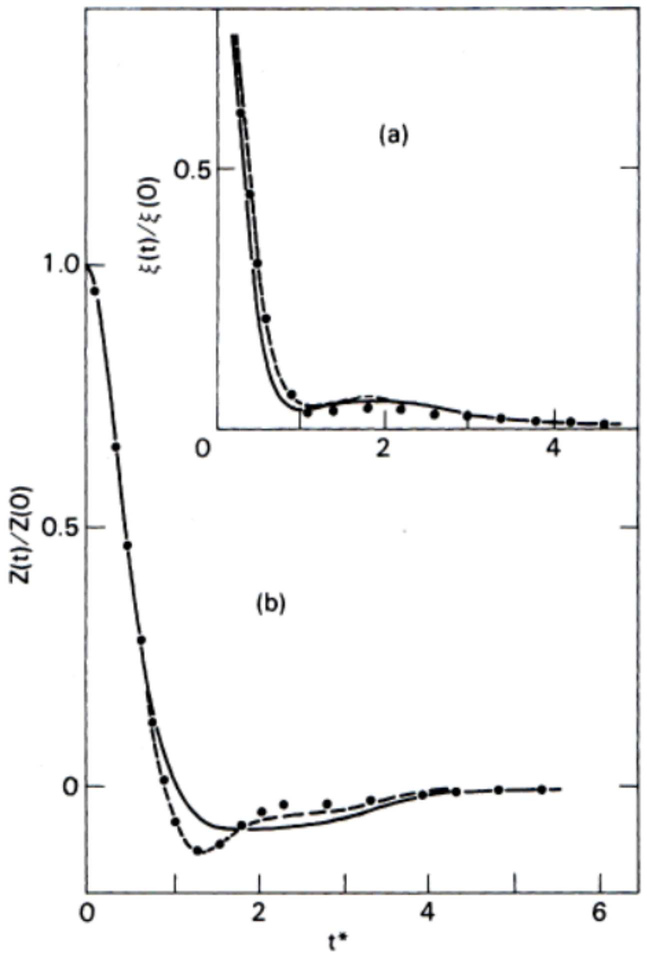


FIG. 9.7. Velocity autocorrelation function and the associated memory function (inset) of the Lennard-Jones fluid near the triple point. The points are molecular dynamics results of Levesque and Verlet (1970), and the curves are calculated from the kinetic theory of Sjögren (1980a) before (full lines) and after (dashed lines) modification of the binary-collision term in the memory function (see text). The unit of time is the quantity τ_0 defined by Eqn (3.3.5). After Sjögren (1980a).